

Characterization of gas emissions and odors upon composting : study of the correlation between the odor concentration and chemical composition

Carlos Andrés Rincon Mejia

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Par

Carlos Andrés RINCON MEJIA

Caractérisation des émissions gazeuses et des odeurs en compostage. Etude de la corrélation entre la concentration d'odeur et la composition chimique des émissions

Thèse présentée et soutenue à Rennes, le 4 avril 2019

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Synthèse des travaux

Les traitements par compostage et/ou méthanisation des déchets et produits résiduaires organiques (PRO) permettant le retour au sol de la matière organique s'inscrivent parmi les modes de gestion que privilégie la directive 2008/98/CE.

Le nombre de plates-formes de compostage et les gisements traités rendent compte de la place des procédés de compostage et de méthanisation. En 2007, un audit commandé par l'ADEME estimait à 820 le nombre de plates-formes de compostage en France parmi lesquelles 100 plates-formes dédiées au traitement des déjections animales. Le gisement de déchets traité et la quantité de composts produits par les 551 plates-formes enquêtées étaient alors estimés à 6 et 2,3 Mt (ADEME, 2007). A ces gisements traités et quantités de composts produits s'ajoutent : i) ceux des plates-formes non enquêtées (100 plates-formes traitant des déjections animales, 15 plates-formes en projet, 25 fermées, 65 plates-formes traitant moins de 1000 t par an de déchets ou traitant en leur sein des ordures ménagères, 57 plates-formes pour lesquelles les informations requises n'ont pu être obtenues), ii) ceux relevant de la gestion de proximité au centre de laquelle se trouve le compostage (620 000 tonnes de déchets de cuisine et 4,5 à 5 Mt de déchets verts)(ADEME, 2018). En 2018, le Club Biogaz estimait à 553 le nombre d'installations de méthanisation en France auxquelles s'ajoutent celles annexées aux stations d'épuration des eaux usées (STEP, 79+) et aux centres de stockage de déchets (156+). Au 1er janvier 2017, le parc d'unités de méthanisation à la ferme comptait 281 unités. Le Plan Energie Méthanisation Autonomie Azote vise 1000 unités de méthanisation à la ferme en 2020 (ADEME, 2017).

Au-delà de la qualité des composts, le statut de produit étant conditionné à leur homologation ou à leur conformité à une norme amendement (NF U 44051, NF U 44095, NF U 42001), c'est également l'activité de compostage, et en particulier relativement aux émissions gazeuses associées, qui fait l'objet d'un encadrement réglementaire. Ces dernières en effet contribuent à l'effet de serre, cas des émissions de méthane (CH_4) et de protoxyde d'azote (N_2O), aux pluies acides, à l'eutrophisation et à l'enrichissement de l'atmosphère en nanoparticules, cas des émissions d'ammoniac (NH_3) et véhiculent des composés odorants tels que l'ammoniac, le sulfure d'hydrogène (H_2S) et des composés organiques volatils (COV) altérant la qualité de vie des riverains des sites de traitement. C'est également la santé des travailleurs au sein de ces sites (Chollot et al., 2018) qui peut être affectée par ces émissions et en particulier celles de NH_3, d'H_2S, de COV et d'odeurs.

En dépit des prescriptions que fixent la loi (arrêté du 27/07/12), « Plus de la moitié des unités de compostage sont concernées par un problème d'odeur » soit « près des 2/3 des tonnages » traités (ADEME, 2007). De fait, les odeurs sont à l'origine de conflits récurrents entre exploitants et riverains des

plateformes. Ces conflits ont conduit plusieurs sites à des arrêts temporaires voire définitifs et font obstacle à l'ouverture de nouveaux (Schlegelmilch et al., 2005 ; Tsai et al., 2008).

En 2005 puis en 2012, l'ADEME soulignait le défaut d'informations relatives aux odeurs émises par les unités de traitement biologiques des déchets, défaut imputable pour partie à la difficulté de caractériser les émissions de composés odorants et en particulier les odeurs alors même que cette caractérisation apparait comme la première étape nécessaire à la réduction de ces émissions et des nuisances associées.

Les travaux décrits ici ont eu pour double objectif de contribuer à combler ces défauts de caractérisation des émissions de composés odorants et des odeurs des unités de traitement biologique des déchets ainsi que de contribuer à une meilleure compréhension des relations entre ces émissions et les odeurs.

Le manuscrit est structuré comme suit :
Introduction
Chapitre 1 : Etat de l'art
Chapitre 2 : Matériels et méthodes
Chapitre 3 : Contribution aux odeurs des différentes étapes de compostage – Cas du traitement d'une boue digérée
Chapitre 4 : Caractérisation des émissions gazeuses et des odeurs en phase active lors du traitement par compostage d'un panel de dix déchets solides et cinq digestats
Chapitre 5 : Prédiction de la concentration d'odeur à partir de la composition des émissions – Cas des émissions en phase active de compostage de six déchets et trois digestats
Conclusions et perspectives

L'ensemble du manuscrit est rédigé en anglais et les Chapitres 3, 4 et 5 sont sous la forme d'articles soumis (Chapitre 4) et publiés (Chapitres 5 et 6). Nous donnons ici un résumé du contenu de chacune de ces parties.

Chapitre 1 : Etat de l'art

Le Chapitre 1 donne un état de l'art des contextes sociétal, environnemental et scientifique de la problématique des odeurs en traitement biologique des déchets et produits résiduaires organiques. Plus précisément, y ont été décrites dans un premier temps les méthodes de caractérisation des odeurs (concentration, qualité, tonalité hédonique et nuisances) ainsi que les principales étapes et opérations (réception-stockage, prétraitement, méthanisation, séparation solide-liquide, phase active, retournements, maturation, criblage) mises en œuvre sur les unités de compostage et de méthanisation. Les processus (biologiques et de transfert) et les conditions à l'origine de ces émissions (forte biodégradabilité, défaut

d'oxygénation et échanges intenses entre matière et phase gazeuse) ont été explicités. Enfin une analyse bibliographique des données, qualitatives et quantitatives, sur les émissions et les odeurs en traitement biologique a été menée. Cette synthèse a mis en évidence i) un défaut d'informations relatives aux émissions et aux odeurs pour l'ensemble des étapes et opérations mises en œuvre en unité de traitement biologique des déchets et PRO, ii) un défaut de standardisation des méthodes et d'exhaustivité des données tant sur les émissions que sur les odeurs en phase active de traitement aérobie des déchets et des PRO ainsi que des résidus issus de leur digestion anaérobie (digestat), et iii) l'intérêt croissant pour la recherche du lien entre odeur et composition chimique et la nécessité d'explorer de nouvelles relations entre ces paramètres.

Chapitre 2 : Matériels et méthodes

Le Chapitre 2 décrit la démarche scientifique et les matériels et méthodes utilisés pour combler les défauts de données tant qualitatives que quantitatives sur les émissions et les odeurs en traitement biologique des déchets.

Le défaut de données d'émission en phase active pour certains déchets, PRO et digestats, a mené à sélectionner puis prélever 15 substrats (10 déchets et 5 digestats) sur 13 sites producteurs ou traitant ces substrats. Ces 15 substrats comptaient 3 résidus issus des activités agricoles (élevages) parmi lesquels 1 digestat, 5 biodéchets (issus de collecte sélective ou d'activités de restauration) dont 2 digestats, 2 déchets verts, 2 boues de STEP dont 1 digestat de boue, 3 fractions organiques d'Ordures Ménagères Résiduaires (OMR) dont 1 digestat (Tableau 1).

Le défaut de standardisation des méthodes a conduit à privilégier une caractérisation des émissions et des odeurs à la source par simulation en pilotes (Fig. 1, 2 et 3) des principales étapes et opérations émettrices en compostage et méthanisation à savoir la réception et le stockage, la phase active de compostage, les retournements en phase active et la maturation.

Les méthodes de prélèvement et d'analyses chimiques (par piégeage acide pour NH_3, par chromatographie et détection électrochimique pour les soufrés et par adsorption puis désorption en GC /MS pour les COV et sensorielles (mesure de la concentration d'odeur par olfactométrie dynamique, Fig. 4) des gaz issus des dispositifs expérimentaux ont été décrites.

La valeur d'activité odorante (OAV) de chaque composé a été obtenue en divisant sa concentration dans l'échantillon par son seuil olfactif (SD). Les valeurs de SD utilisées ont été celles rapportés par Nagata (2003) et Van Gemert (2011). La variabilité des valeurs de SD dans la littérature a conduit à effectuer sa mesure par olfactométrie dynamique pour 15 composés. Ces derniers comptaient des

molécules détectées fréquemment et des substances avec de faible SD, tels que les CSV, la triméthylamine (TMA) et la 2,3-butanedione.

Les SD obtenus aux Chapitres 4 et 5 et utilisés au chapitre 3 ont été corrigés par la mesure pour quelques composés de leur taux de recouvrement. Certains composés peuvent en effet s'adsorber à la surface des poches nalophan, cette adsorption conduisant à surestimer la concentration des composés en phase gazeuse et donc leurs SD (Hansen et al., 2011; Kasper et al., 2018). La correction a dès lors consisté en i) le suivi cinétique de la concentration dans les poches des dits composés, suivi de 3 à 6 heures après remplissage de la poche et couvrant la période de mesure de CO par olfactométrie, puis ii) en la mesure par olfactométrie de la concentration d'odeur des échantillons gazeux contenant les composés et iii) en le calcul de leur SD.

Enfin l'ensemble des approches statistiques utilisées pour modéliser les émissions et les odeurs ont été expliquées.

Chapitre 3 : Contribution aux odeurs des différentes étapes de compostage – Cas du traitement d'une boue digérée

Le Chapitre 3 consiste en l'article soumis dans le journal *Waste Management* sous le titre : « *Odor generation patterns during different operational composting stages of anaerobically digested sewage sludge.* » Carlos Andrés Rincón, Amaury de Guardia, Annabelle Couvert, Isabelle Soutrel, Stevan Guezel, Camille Le Serrec.

Les traitements par compostage et méthanisation suivie d'un compostage ont en commun plusieurs étapes et opérations appliquées à la matière parmi lesquelles la réception et le stockage, la phase active en compostage, les retournements de la matière en phase active et la maturation. Les informations limitées des inventaires d'émissions et d'odeurs pour certaines de ces étapes de traitement ont été mises en évidence dans la revue de littérature réalisée au Chapitre 1. En fait, à l'exception de la phase active de compostage, peu d'études, aucune s'agissant des digestats, ont évalué ces émissions au cours des autres étapes et opérations. Ce défaut de données peut conduire à sous-estimer les nuisances olfactives associées à ces traitements. Il compromet par ailleurs la pertinence de sélection des dispositifs de réduction de ces nuisances.

Les travaux menés dans le Chapitre 3 ont eu pour objectifs de caractériser, qualitativement et quantitativement, les émissions et les odeurs en stockage, en phase active, au cours des retournements et en maturation lors du traitement par compostage d'une boue digérée (ADS).

Trois dispositifs expérimentaux ont été utilisés pour simuler ces étapes : i) un pilote isolé de volume 300 L pour simuler la phase active et dont la configuration permet une aération forcée de la matière par

injection d'air à la base de cette dernière (Fig. 1), ii) le même pilote pour simuler le stockage et la maturation par injection d'air à la seule surface de la matière (Fig. 1) et iii) un dispositif pour simuler le retournement de la matière consistant en quatre récipients en plastique, hermétiques, de volume 10L, reliés en série et alimentés par un flux d'air de balayage, la simulation du retournement étant obtenue par dépose de la matière dans les récipients puis agitation de ces derniers (Fig. 2). La simulation du compostage a débuté par le stockage d'ADS pendant 8 jours, le débit d'air appliqué en surface d'ADS étant de 55,8 L h^{-1} (0,149 m^3 h^{-1} m^{-2}). Ensuite, le substrat a été mélangé avec du structurant (rapport massique copeaux de bois/boues = 0,55) et composté durant 30 jours par application d'une aération forcée positive (279 L h^{-1}). Deux retournements de la matière ont été effectués aux 8ème et 21ème jours de la phase active. Quatre échantillons du mélange en compostage ont alors été prélevés lors de la vidange du réacteur et placés dans le dispositif de simulation des retournements, les débits d'air de balayage de la surface étaient respectivement de 669 et 892 L h^{-1}. Une fois la phase active terminée, le mélange a été placé en maturation pendant 27 jours. Le débit d'air appliqué en surface du mélange était 56,2 L h^{-1} (0,15 m^3 h^{-1} m^{-2} de surface de réacteur).

Tout au long du traitement à l'exception des retournements, les concentrations en oxygène, dioxyde de carbone, méthane et protoxyde d'azote des gaz entrants et sortants ont été mesurées en continu. L'ammoniac émis a été piégé en solution acide et les pièges ont été changés aux dates d'échantillonnage des gaz sortants i.e. tous les deux à trois jours. Les échantillons de gaz ont été collectés dans des poches de nalophan. Une partie du contenu des gaz échantillonnés a été adsorbé sur des tubes carbotraps afin de concentrer les composés organiques volatils. Les COV piégés ont ensuite été désorbés thermiquement, puis séparés et quantifiés par chromatographie couplée à un spectromètre de masse (TD-GC/MS). La quantification des composés soufrés volatils (CSV) a été effectuée par chromatographie en phase gazeuse couplée à un détecteur électrochimique (MEDOR). La mesure de la concentration d'odeurs (CO) en unités d'odeur européennes (OU_E m^{-3}) a été réalisée par olfactométrie dynamique.

Dix-neuf composés ont été identifiés et quantifiés au cours des différentes étapes du compostage d'ADS (Tableau 3). Ces composés ont été regroupées en six familles chimiques i.e. les composés contenant de l'azote, les soufrés, les cétones, les alcools, les terpènes et les acides organiques volatils. Les émissions d'ammoniac représentent 55,5% du total des émissions, celles de CSV i.e. diméthyle disulfure, sulfure d'hydrogène, diméthyle sulfure et méthyle mercaptan, 20,6%. Le stockage et la phase active ont été les phases les plus émettrices, les émissions au cours de ces phases représentant respectivement 16 et 77% du total des émissions (35 mg kg^{-1}ADS). 40% des émissions se sont produites au cours des 8 premiers jours de phase active.

Le débit d'odeur (OER), produit de la concentration d'odeur (CO) par le débit d'air humide sortant, a été calculé à chaque date à laquelle le gaz sortant a été prélevé (Fig. 5). Un premier maximum de débit d'odeur, 56,6 OU_E h^{-1} kg^{-1}ADS, a été observé en début de phase active. Ce pic est vraisemblablement

attribuable au stripage des molécules réduites formées au cours du stockage et en début de phase active, stripage favorisé par le mélange de la boue au structurant puis l'application d'une aération forcée et l'accroissement de la température de la matière. Un deuxième pic d'OER, 317 OU_E h^{-1} kg^{-1}ADS, 5 fois supérieur à celui mesuré en début de phase active, a été observé lors du premier retournement de la matière. L'intensité de ce pic s'explique par le passage en phase gazeuse de molécules réduites produites au cours de la période précédant le retournement dans des fractions de matière mal aérées. Cette intensité traduit également une contribution potentielle élevée des étapes de retournements aux nuisances olfactives associées au traitement biologique des déchets. Après le 1er retournement, le débit d'odeur a décru rapidement pendant 24h puis plus lentement, à l'exception d'une légère re-croissance après le second retournement, pour se stabiliser autour de 30 OU_E h^{-1} kg^{-1}ADS en fin de phase active. En maturation, l'absence d'application d'une aération forcée au sein de la matière et la plus grande stabilité de cette dernière expliquent les faibles débits d'odeur mesurés i.e. autour de 0,18 OU_E h^{-1} kg^{-1}ADS.

L'intégration sur le temps du débit d'odeur permet de calculer la quantité d'odeur émise par unité de masse initiale de déchet i.e. le facteur d'émission d'odeur (OEF) exprimé en OU_E kg^{-1} d'ADS. Pour l'ensemble du traitement, la quantité d'odeur mesurée a été de 12143 OU_E kg^{-1} d'ADS. Le stockage, la phase active et le premier retournement ont contribué respectivement à hauteur de 5, 82 et 5% à OEF.

Pour chaque échantillon de gaz prélevé, la VAO de chacun des composés quantifiés a été calculée (VAO (adimensionnel) = CC / SD avec CC concentration chimique du composé dans l'échantillon et SD, seuil de détection olfactif du composé) en vue d'appréhender les composés les plus contributeurs des odeurs. Les CSV et l'acide acétique ont été identifiés comme les principaux contributeurs des odeurs (Fig. 8A). Néanmoins, il a été mis en évidence un changement de composition odorante au fur et à mesure du traitement (Fig. 8B). Ainsi, le méthyle mercaptan, le diméthyle disulfure, le diméthyle sulfure, d'odeurs caractéristiques celles du choux en putréfaction et de l'ail, prédominaient au stockage, en début de phase active et au premier retournement alors qu'au-delà ce sont le sulfure d'hydrogène et l'acide acétique, dont les odeurs caractéristiques sont celles des œufs pourris et du vinaigre d'alcool, qui étaient les contributeurs majeurs.

Enfin, une analyse en composante principale (ACP) expliquant 77% de la variabilité de l'ensemble de données des CO et VAO a mis en évidence chacune des étapes du traitement. L'ACP a montré par ailleurs que les composés les plus contributeurs des odeurs dont chacune était responsable étaient relativement spécifique de l'étape et de fait en constituait une signature olfactive. Par conséquent, l'ACP pourrait constituer un outil puissant dans les programmes d'enquête sur les odeurs des sites de traitement des déchets.

Chapitre 4: Caractérisation des émissions gazeuses et des odeurs en phase active lors du traitement par compostage d'un panel de dix déchets solides et cinq digestats

Les travaux effectués ont fait l'objet d'un article publié dans *Journal of Environmental Management* (233 p. 39-53, 2019) sous le titre: « *Chemical and odor characterization of gas emissions released during composting of solid wastes and digestates.* » Carlos Andrés Rincón, Amaury de Guardia, Annabelle Couvert, Sophie Le Roux, Isabelle Soutrel, Mylène Daumoin, Jean Claude Benoist.

La contribution des premiers jours de phase active à l'émission d'odeur a été mise en évidence au sein du Chapitre 3 lors du traitement d'un digestat de boues. Un maximum d'émission d'odeur (OER) a en effet été observé en début de phase active, maximum confirmé par un facteur d'émission d'odeur (OEF) élevé sur cette première période de traitement. A l'instar de ces travaux, la phase active de compostage est considérée comme l'une des étapes les plus émettrices des traitements biologiques des déchets et produits résiduaires organiques. Au cours de celle-ci, sous aération naturelle ou forcée, les matières organiques sont transformées par les micro-organismes en conditions aérobies mais également anoxiques voire anaérobies. Les métabolites de dégradation de la matière contribuent à l'effet de serre (CO_2, CH_4 et N_2O), aux pluies acides, à l'eutrophisation des milieux, à la formation de nanoparticules (NH_3) ou sont à l'origine de nuisances olfactives (NH_3, H_2S, COV, CSV). S'agissant des nuisances olfactives, celles-ci impactent le bien-être voire la santé des travailleurs mais également celui des résidents riverains. Certaines substances toxiques voire cancérigènes seraient émises lors des traitements par aération forcée (Cadena et al., 2009). Les nuisances olfactives ont également des conséquences économiques tant pour les exploitants des sites de traitement que pour les riverains dont la valeur des biens immobiliers peut être dévalorisée. La première étape pour faire face aux problèmes susmentionnés consiste en la caractérisation et la compréhension des modes de génération des émissions et des odeurs en compostage et en particulier en phase active. Ces données de caractérisation sont en effet indispensables à la définition des solutions curatives de réduction des émissions. Ce sont également des intrants nécessaires à la modélisation de leur dispersion dans l'atmosphère.

De fait, la phase active a fait l'objet de quelques travaux ayant pour objectif la caractérisation des émissions et odeurs associées au traitement de différents déchets i.e. la fraction fermentescible des ordures ménagères (Maulini-Duran et al., 2013b; Scaglia et al., 2011; Schiavon et al., 2017), des ordures ménagères résiduelles (Eitzer, 1995; Rodríguez-Navas et al., 2012), des déchets alimentaires (Komilis et al., 2004), des boues d'épuration (Durme et al., 1992; Maulini-Duran et al., 2013a). Pour autant, les travaux effectués, selon des méthodologies différentes et dans des conditions différentes, chacun se limitant qui plus est à quelques substrats et quelques composés gazeux, ne permettent pas d'aboutir à une caractérisation rigoureuse et exhaustive des émissions et des odeurs en phase active. Ces lacunes dans les connaissances sur les émissions provenant du compostage se traduisent par exemple par l'absence de facteurs d'émission de polluants ou d'odeurs ou encore un nombre limité de types de produits résiduaires organiques étudiés.

Ainsi seuls quelques travaux se sont intéressés aux émissions des digestats et les ont comparées à celles des substrats bruts (Maulini-Duran et al., 2013a).

Les travaux de recherche menés au Chapitre 4 ont eu pour objectif de caractériser de manière exhaustive les composés volatils et les odeurs émis par différents déchets et digestats lors de leur traitement en phase active sous aération forcée, dans des conditions contrôlées et comparables.

Dix déchets et cinq digestats (Tableau 1) issus des différentes grandes familles de déchets (ordures ménagères résiduelles, biodéchets, déchets verts, boues d'épuration et effluents d'élevage) ont été prélevés sur treize sites producteurs ou traitant ces déchets par compostage ou méthanisation. La période écoulée entre les premiers et les derniers prélèvements effectués a été de 14 mois. Stockés à -20°C après prélèvement, ces déchets étaient placés en décongélation à température ambiante 48 à 72 heures avant de les placer en phase active.

Certains déchets et digestats ont été mélangés avec des plaquettes de bois calibrées avant compostage. Le ratio massique d'incorporation de plaquettes au déchet était compris entre 0,4 et 1,1 (kg/kg). Le mélange a ensuite été introduit dans un réacteur de simulation de compostage tel que décrit au Chapitre 3. Une fois le réacteur fermé et l'instrumentation de suivi en place, une aération forcée positive a été appliquée consistant en un premier taux, faible, pendant 48h puis en l'application d'un taux plus élevé ensuite et ceci jusqu'à la fin du traitement i.e. à environ 30 jours. Des retournements de la matière par vidange du réacteur ont été appliqués aux 10 et 20ème jours. Pour chaque déchet, le taux d'incorporation de structurant et le taux d'aération appliqué après 48h ont été fixés sur la base des taux appliqués sur sites réels pour traiter ces déchets ainsi que de l'expertise d'Irstea en vue d'une production d'odeur qui soit ne ni exagérément faible ni exagérément élevée (Blazy et al., 2014; de Guardia et al., 2010). Dans ce chapitre dédié à la caractérisation des émissions et des odeurs en phase active, chaque expérimentation a consisté en le chargement de trois réacteurs identiques, chacun rempli d'un déchet ou d'un mélange déchet-structurant distinct des deux autres. Cinq expérimentations ont donc été mises en œuvre.

Les gaz sortant ont été échantillonnés et analysés, NH_3 par absorption dans une solution d'H_2SO_4 puis stripage à chaud, les CSV par chromatographie dédiée (MEDOR, voir Chapitre 2) enfin les COV par TD-GC/MS. La contribution chimique de chaque composé émis a ensuite été obtenue en pourcentage (PCi, %) en divisant le cumul émis du composé par le cumul des masses émises par l'ensemble des composés. De même, les échantillons de gaz ont été analysés par olfactométrie dynamique afin de mesurer la concentration d'odeur (CO), les débits d'odeur (OER) et les facteurs d'émission d'odeur (OEF) conformément à la norme NF EN 13725.

Soixante composés ont été identifiés tout au long des expériences de compostage. Ces substances appartenaient à neuf catégories chimiques, à savoir les composés soufrés, les terpènes, les cétones, les

alcools, les alcènes, les composés azotés, les hydrocarbures aromatiques, les acides et les esters. Il convient de mentionner que certains des déchets solides compostés, tels que les déchets alimentaires, les boues d'épuration et les déchets agricoles, ont présenté des cumuls d'émissions très élevés, allant de 3464 à 28395 mg $kg^{-1}MO_0$, tandis que les digestats présentaient des cumuls plus faibles variant de 230 à 1090 mg $kg^{-1}MO_0$.

Les types de molécules détectées dans les effluents ont été directement associés à la nature des substrats compostés. En effet, les résultats ont montré que les matrices organiques contenant des fruits, des légumes, des feuilles, des broussailles et des déchets alimentaires tels que des biodéchets, des déchets ménagers et des déchets verts généraient des émissions de gaz riches en terpènes et en composés oxygénés (alcools, acides, esters et cétones) avec une PC_i fluctuant entre respectivement 21 à 90% et 9 à 71%. Les émissions de terpènes étaient également liées au matériau lignocellulosique utilisé comme agent structurant. Le limonène et l'alpha-pinène ont été les terpènes qui sont apparus le plus fréquemment lors du compostage, résultant vraisemblablement de l'élimination de molécules déjà contenues dans les déchets ou du processus de décomposition de matières végétales par dégradation bactérienne de la lignine et de la cellulose (Eitzer, 1995).

D'autres déchets solides et PRO présentant de faibles rapport massique carbone sur azote (C/N), tels que les déchets agricoles (fumier de dinde et fraction solide du lisier de porc), les boues d'épuration et les digestats, ont généré d'importantes émissions d'ammoniac (PC_i = 57-93%). Cela s'explique d'une part par le fait que les déjections animales et les digestats contiennent des quantités importantes de NH_4^+/NH_3 et qu'une fraction de leur azote organique est ammonifié lors du traitement.

Une attention particulière a été accordée à la mesure des débits d'odeurs (OER) et au calcul des facteurs d'émission d'odeurs (OEF) en réponse au défaut de telles grandeurs dans la littérature. Les résultats ont indiqué que les déchets solides et les digestats avaient des profils d'OER similaires, marqués par une augmentation de ceux-ci au cours des 15 premiers jours du processus aérobie. Cette augmentation des valeurs d'OER a coïncidé avec la phase thermophile dans laquelle la fraction fermentescible des déchets facilement disponible aux microorganismes est décomposée. Les OER maximaux pour les déchets solides étudiés allaient de 829 à 27306 $OU_E\ h^{-1}\ kg^{-1}MO_0$, alors que les digestats présentaient des OER maximaux qui fluctuaient de 22 à 115 $OU_E\ h^{-1}\ kg^{-1}MO_0$. Enfin, les OER ont tendance à chuter à la fin du processus lorsque l'activité microbienne ralentit.

Le processus de compostage des déchets solides a révélé des OEF élevés allant de 3089 à 65 $OU_E\ g^{-1}MO_0$ tandis que le post-traitement aérobie des digestats présentait des OEF faibles variant de 30,5 à 8,6 $OU_E\ g^1\ MO_0$. Cette différence entre les OEF peut s'expliquer par le fait que les digestats étaient auparavant stabilisés par un processus de digestion anaérobie réduisant ainsi leurs potentiels d'émission de substances odorantes tout au long de la dégradation aérobie. De plus, les digestats étaient généralement

compostés avec des copeaux de bois, ce qui diminuait la quantité de matière organique facilement dégradable présente dans le mélange à composter (Maulini-Duran et al., 2013a) et réduisait l'occurrence de zones anaérobies, généralement liées aux émissions de composés dégageant des odeurs.

Les principaux contributeurs olfactifs des émissions produites en phase active ont été déterminés sur la base du calcul de la VAO pour chacun des composés i constitutifs des émissions. La contribution de i aux odeurs émises tout au long du traitement de chacun des déchets, POi (%), a été calculée en faisant le ratio de la VAO la plus élevée enregistrée pour le composé au cours du traitement, $VAO_{max\text{-}i}$, par la somme des VAO_{max} de l'ensemble des composés $SVAO_{max}$: POi (%) = $100*VAO_{max\text{-}i} / SVAO_{max}$.

Pour tous les substrats compostés, les CSV, dont les PO_i étaient compris entre 54 et 99%, sont apparus comme les principaux contributeurs des odeurs. Cette contribution majeure s'explique par leur volatilité élevée, leur faible seuil olfactif ainsi que par l'ensemble des conditions favorisant leur formation et émission i.e. défaut d'oxygénation liée à un défaut de structurant et paradoxalement taux d'aération trop élevé (Blazy, 2014). Les principaux CSV contribuant aux nuisances olfactives étaient le méthyle mercaptan, l'éthyle mercaptan et le sulfure d'hydrogène représentant entre 34% et 95% de $SVAO_{max}$. Selon nos résultats, le méthane thiol est l'agent le plus contributeur aux odeurs en compostage, puisqu'il est responsable de VAO_{max} dans 73% des expériences de simulation de compostage effectuées. H_2S est le composé le plus contributeur des odeurs associées au traitement des refus de lisier de porc, des digestat de déchets ménagers et des déchets verts, tandis que l'éthyle mercaptan présentait le plus grand VAO_{max} lors du compostage des déchets alimentaires ménagers. Puisque les CSV ont été identifiés comme les principaux composés odorants émis en phase active, certaines technologies de réduction de ces CSV ont été décrites en appendix de l'article.

Enfin, il a été constaté que d'autres composés pouvaient également contribuer aux odeurs en phase active. C'est le cas de la triméthylamine (TMA) dont l'odeur est celle du poisson en putréfaction et dont le PO_i était de 7% lors du traitement en phase active du refus de lisier de porc et de 39% dans le cas du fumier de dinde. C'est également le cas du limonène, odeur de citron, de PO_i égal à 42,5% lors du traitement des déchets de cuisine (fraction crue des déchets alimentaires) et de la 2,3-butanedione, odeur de beurre rance, de PO_i égal à 23,4% lors du traitement des déchets de repas (fraction cuite des déchets alimentaires). Pour autant la perception singulière de chacun de ces composés n'est pas évidente. Alors que la TMA et la 2,3-butanedione contribuent à altérer le caractère hédonique des odeurs émises en traitement de refus de lisier et de la fraction cuite des déchets alimentaires, le limonène contribuerait à améliorer l'impact hédonique de l'odeur émise lors du traitement de la fraction crue des déchets alimentaires.

Chapitre 5 : Prédiction de la concentration d'odeur à partir de la composition des émissions – Cas des émissions en phase active de compostage de six déchets et trois digestats

Le travail mené au Chapitre 5 a fait l'objet d'un article publié dans le journal *Atmospheric environment* (222 pp. 1-12, 2019) sous le titre « *Odor concentration (OC) prediction based on odor activity values (OAVs) during composting of solid wastes and digestates.* » Carlos Andrés Rincón, Amaury de Guardia, Annabelle Couvert, Dominique Wolbert, Sophie Le Roux, Isabelle Soutrel, Guillaume Nunes.

L'approche sensorielle des odeurs recèle un certain nombre de limites que sont : i) un échantillonnage circonscrit dans le temps, ii) des échantillons dont les caractéristiques sensorielles évoluent rapidement imposant un délai court entre échantillonnage et caractérisation, iii) la lourdeur des protocoles expérimentaux se fondant sur la perception de l'odeur par un groupe de panelistes et le risque associé de subjectivité de la perception (Hansen et al., 2016; Wu et al., 2017), iv) des coûts élevés tant en fonctionnement qu'en investissement (Laor et al., 2014), v) une approche souvent empirique tant de la qualité que du caractère hédonique de l'odeur, vi) l'absence d'identification et de quantification des composés les plus contributeurs, requise par exemple pour définir une solution curative s'il s'agit d'un effluent canalisé etc… L'approche chimique des odeurs vise à rendre compte des ressentis olfactifs en s'affranchissant des limites de l'approche sensorielle. Elle se fonde notamment sur la caractérisation des molécules constitutives du mélange odorant et en la corrélation des descripteurs de l'odeur (concentration, qualité, tonalité) aux caractéristiques de ces molécules.

La concentration d'odeur d'un gaz odorant est définie comme le facteur de dilution du gaz au seuil de perception de l'odeur. Pour un gaz ne contenant qu'un composé odorant, le facteur de dilution correspond à la VAO du composé définie comme le rapport de la concentration du composé sur son seuil de détection. Dans le cas d'un gaz contenant plusieurs composés odorants, la corrélation entre la composition du gaz et sa concentration d'odeur a fait l'objet de nombreuses investigations. L'incidence de la concentration d'odeur sur le ressenti de nuisances que met en avant l'approche règlementaire des nuisances olfactives (décret du 27/07/12) explique pour partie cet intérêt de corréler la concentration à la composition du mélange odorant. Pour autant la concentration d'odeur ne rend pas compte des autres descripteurs de l'odeur également déterminants du ressenti de nuisance que sont sa qualité et sa tonalité hédonique. Il est néanmoins permis de penser que la maîtrise de la corrélation entre composition et concentration d'odeur est une étape utile à celle ultérieure de corréler la composition aux autres descripteurs de l'odeur i.e. sa qualité et sa tonalité hédonique.

Une première approche de la corrélation entre composition et concentration d'odeur a consisté à construire des modèles de prédiction avec les VAO des composés constitutifs des mélanges gazeux. Ainsi des corrélations linéaires entre la concentration d'odeur, mesurée par olfactométrie (CO) et, la somme des VAO, VAO_{um}, et la VAO la plus élevée, VAO_{max}, des composés odorants contenus dans les mélanges, ont

été évaluées (Blazy et al., 2015; Capelli et al., 2012; Wu et al., 2017). Ces modèle linéaires simples basés sur des substituts d'odeur ont généralement donné de bons résultats pour expliquer la variabilité de CO (R^2= 0,83-0,91). Cependant, ces études ont montré la sous-estimation de CO prédite possiblement liés à des effets olfactifs interactifs (synergie et antagonisme), de la forte variation des ensembles de données des seuils de détection olfactifs (SD), et des limitations concernant le nombre d'échantillons de gaz analysés.

Parker et al. (2012) ont mené une étude pionnière dans le but de développer des modèles multivariés permettant de prédire la concentration d'odeur d'un effluent gazeux d'élevage à partir des VAO des composés odorants de l'effluent. Selon cette étude, des modèles de régression linéaire multiple, permettant d'intégrer les interactions possibles entre les substances odorantes, peuvent améliorer la prédiction de CO, R^2= 0.66-1. Peu de travaux rendent compte de l'utilisation de méthodes statistiques multivariées puissantes telles que les régressions des moindres carrés partiels (PLS) pour étudier la corrélation entre CO et les VAO.

Dans le cas du traitement biologique des déchets, le lien entre VAO et CO a à peine été abordé dans la littérature. De plus, alors que comme indiqué au Chapitre 4, la composition et la concentration d'odeur des émissions peuvent varier de façon significative d'un déchet à l'autre, les modèles de prédiction de CO à partir des VAO n'ont en général été testés que sur un seul déchet.

Les travaux retranscrits dans ce chapitre ont eu pour objectifs de poursuivre les recherches sur la prédiction de CO d'une émission à partir des VAO des composés contenus dans l'émission. Les données expérimentales utilisées ont été celles obtenues dans le cadre de la caractérisation chimique et olfactive des émissions, en phase active de compostage, de six déchets et trois digestats (Chapitre 4). Quatre-vingt-douze échantillons gazeux ont été caractérisés.

La corrélation de CO à VAO_{max} et VAO_{sum} a été ré-investiguée, des modèles de régressions des moindres carrés partiels, PLS) ont été développés et leurs performances comparées à celles des modèles linéaires simples. Les résultats des évaluations des odeurs et des analyses de régression ont été exploités en vue d'une meilleure compréhension de l'origine des odeurs lors du compostage des déchets solides et PRO.

Étant donné que CO et VAO sont distribués de façon logarithmique (Akdeniz et al., 2012; Hansen et al., 2016), elles ont été exprimées en Log avant d'effectuer les analyses de régression. La capacité de VAO pour prédire CO a été en premier lieu évaluée à l'aide des modèles de régression linéaire simple. Deux modèles linéaires simples ont été testés: i) Log (VAO_{max}) = βLog (CO) et ii) Log (VAO_{sum}) = βLog (CO).

Par la suite, une régression PLS a été effectuée avec The Unscrambler X version 10.5 (CAMO, Norvège) pour prédire CO en fonction des VAO des substances odorantes identifiées. À cette fin, les

données obtenues lors des analyses sensorielles et chimiques ont été divisées en un ensemble d'apprentissage et un ensemble de prévision. Des modèles d'étalonnage ont été construits sur la base de l'échantillon d'apprentissage qui a été validé dans un premier temps par validation croisée segmentée. Leurs puissances prédictives ont été testées en utilisant les observations de l'échantillon de prévision. Le coefficient de détermination (R^2), l'erreur quadratique moyenne de validation croisée (RMSECV) et l'erreur quadratique moyenne de prévision (RMSEP), ont permis d'évaluer la performance et la robustesse des modèles (Gutiérrez et al., 2015). Un premier modèle de régression PLS a été développé avec 22 odorants quantifiés. Ensuite, un processus itératif de sélection des variables a été mis en place de façon à éliminer les variables non statistiquement significatives sur la base de leur variabilité tout au long du processus de validation croisée (Hansen et al., 2016).

Au total, 22 composés volatils quantifiés ont présenté des concentrations dépassant au moins une fois leurs SD et ont donné des VAO supérieures à un. Le méthanol, NH_3, H_2S, l'alpha-pinène, le disulfure de diméthyle (DMDS), l'acide acétique et le limonène ont été détectés dans plus de 70% des échantillons de gaz analysés. CO mesurée au cours du traitement aérobie des substrats a montré une médiane de 4381 OU_E m^{-3} et une plage interquartile de 1962-17323 OU_E m^{-3}. Il convient de mentionner que les VAO calculées pour les CSV, la TMA, et la 2,3-butanedione auraient pu être sous-estimées à faibles concentrations, ces composés ayant des SD plus faibles que leurs limites de détection. Cependant, il a été démontré que cette erreur n'affecte pas de façon considérable le calcul de VAO_{max} et de VAO_{sum}.

Pour les 92 échantillons de gaz analysés, les VAO_{max} étaient celles d'H_2S (51,1%), du CH_3SH (33,7%), du limonène (4,3%), de l'acide acétique (4,3%) et d'autres composés tels que le disulfure de diméthyle (2,2%), la 2,3 -butanedione (2,2%) et l'éthanethiol (2,2%). En d'autres termes, les CSV responsables de 89% des des VAO_{max} sont les principaux contributeurs des odeurs en phase active de compostage des déchets solides et des digestats. Le modèle linéaire se fondant sur VAO_{max} permet d'expliquer 67% de la variance mesurée de CO ($p < 0,0001$) en donnant une fonction $Log(VAO_{max}) = 0,93\ Log(CO)$, relativement proche de l'intervalle de confiance de 95% et présentant un comportement similaire à l'hypothèse idéale de $Log(VAO_{max})$ égal à Log(CO) (Fig. 1). Dans le cas de VAO_{sum}, la fonction linéaire $Log(VAO_{sum}) = 0,97\ Log(CO)$ est légèrement meilleure que celle se fondant sur VAO_{max} ($R^2 = 0,73$, $p < 0,0001$). Pour autant, les deux modèles conduisent à une sous-estimation des valeurs de CO pour 63% des échantillons de gaz analysés. En effet, les CO prédites par VAO_{sum} et VAO_{max} étaient en moyenne inférieurs de 11 à 13% aux CO mesurées. Les causes possibles de cette sous-estimation sont i) l'omission d'effets interactifs synergiques, antagonistes et même neutralisants entre les substances odorantes, ii) les incertitudes associées aux réponses du panel telles que les différences de sensibilité aux odeurs des évaluateurs, et iii) les pertes de certains composés lors du stockage des échantillons de gaz et au sein de l'olfactomètre. Malgré cette complexité inhérente à la mesure des odeurs, la corrélation linéaire modérément forte ($R^2 = 0,67$-$0,73\%$, $p < 0,0001$) obtenue entre ces substituts d'odeurs et OC suggère qu'ils

pourraient fournir une estimation préliminaire des odeurs émises en phase active avec malgré tout un certain niveau d'incertitude.

Un premier modèle PLS a été développé et validé en prenant en compte tous les odorants quantifiés. Ce modèle de régression multiple a montré une puissance de prédictibilité modérée lors de la validation croisée et de la validation de prévision (R^2_{CV}= 0,67; R^2_{Predi}= 0,67) car il tenait compte de variables non pertinentes et de bruits de fond interférant dans la prédiction de CO. Par conséquent, un deuxième modèle a été construit en supprimant les variables dont les coefficients de corrélation conservaient une variance élevée tout au long du processus de validation croisée. Le modèle PLS résultant de ce processus de sélection s'est ainsi réduit à dix substances odorantes et a permis d'expliquer 74% de la variance de CO lors de la validation croisée et 76% de la variance de CO lors de la validation avec l'échantillon de prévision (Fig. 4 et Fig. 5). Selon l'analyse de régression PLS, les CSV étaient fortement corrélées à CO et montraient les coefficients de régression les plus élevés (H_2S, CH_3SH et DMDS) (Fig. 2 et Fig. 3) confirmant ainsi les résultats obtenus avec VAO_{max}. Les alcools étaient la seule famille chimique présentant des coefficients de régression négatifs. Ce résultat suggère un possible effet antagoniste du 3-méthyl-1-butanol et de l'éthanol sur la perception des odeurs; Cependant, des expériences sensorielles doivent être menées pour valider cette hypothèse.

Enfin, 50% des valeurs de CO prédites par le modèle PLS ont été sous-estimées, elles étaient en moyenne 7% inférieures aux CO mesurées. Cela signifie que le modèle PLS développé a permis de mieux prédire la CO mesurée avec moins de sous-estimation moyenne que VAO_{max} (13%) et VAO_{sum} (11%). De la même manière, les résultats ont montré que les prévisions de CO fournies par le modèle PLS étaient moins dispersées autour des limites de l'intervalle de confiance de 95% que celles obtenues par les substituts d'odeur. Il convient de souligner que l'applicabilité du modèle PLS développé doit être vérifiée en élargissant le processus de validation avec des nouveaux ensembles d'échantillon de prévision.

Conclusions et perspectives

Les émissions gazeuses au cours de quatre étapes opérationnelles du compostage d'un digestat ont été collectées et analysées par voie chimique et par olfactométrie dynamique. Les profils des débits d'odeurs (OER) tout au long du processus ont mis en évidence deux événements critiques relativement à l'émission d'odeurs: les premiers jours de phase active de compostage et le retournement de la matière. L'OER a ensuite tendance à chuter. Les résultats ont également montré que cette variation du débit d'odeur était conjuguée à une variation des molécules à l'origine des stimuli olfactifs. Une analyse ACP, rendant compte de 77% de la variabilité des valeurs de concentration d'odeur (OC) et d'activité odorante (VAO), et le calcul des VAO ont montré que les composés soufrés volatils (CSV) étaient les principaux contributeurs des odeurs quelle que soit l'étape de compostage.

Les composés volatils et les émissions d'odeurs tout au long de la phase active de compostage de différents déchets solides et digestats ont également été caractérisés. Les résultats obtenus ont montré que la composition chimique et le potentiel olfactif des émissions de gaz en phase active dépendaient fortement de la nature des déchets compostés. Les déchets bruts présentaient des facteurs d'émissions gazeuses et d'odeurs plus élevés que les substrats préalablement digérés par voie anaérobie. Qu'il s'agisse d'un déchet brut ou digestat, les composés soufrés volatils sont apparus comme les principaux contributeurs des odeurs émises en phase active.

Le dernier chapitre du manuscrit a été consacré à l'analyse de la prédictibilité de CO par une caractérisation chimique qualitative et quantitative des émissions. Les résultats ont montré que les substituts d'odeur se fondant sur la VAO, VAO_{max} et VAO_{sum}, étaient modérément bien corrélés à CO mais de façon moindre que les modèles de régression des moindres carrés partiels (PLS). Le modèle PLS développé a permis de réduire la sous-estimation de la CO ainsi que de réduire les écarts à l'intervalle de confiance de 95% des mesures olfactométriques (EN 13725). De même, ces derniers résultats ont corroboré le rôle central des CSV dans la contribution aux odeurs et ont conduit à s'interroger sur la contribution d'autres molécules telle que par exemple les alcools.

Les travaux menés dans cette thèse ont ouvert la porte à de nouvelles questions de recherche. Les travaux futurs devraient notamment :

- investiguer pour d'autres déchets ou PRO la contribution aux odeurs des différentes étapes d'un traitement biologique, ainsi que de compléter les dites étapes par celles du criblage, de la séparation solide-liquide et de l'épandage,
- investiguer l'intérêt du point de vue des émissions d'odeur à co-composter des substrats à forts facteurs d'émission à des substrats à faibles facteurs d'émission,
- compléter le panel des déchets et digestats dont les émissions ont été caractérisées, notamment par la caractérisation des émissions de déchets contenant des graisses. La création d'une base de données en ligne des OEF en compostage et méthanisation serait utile aux concepteurs et exploitants des sites de traitement biologique des déchets ainsi qu'aux institutionnels (ICPE),
- étudier la pertinence des modèles développés pour prédire CO en tant que données d'entrée des modèles de dispersion des odeurs.

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General introduction

Solid waste generation has increased exponentially as a result of the population growth, massive global consumption and unmeasured exploitation of natural resources. Approximately 2.1 billion tons of waste was generated in 2016 in the world, and it is expected to attain the 3.4 billion tons per year in 2050 (Kaza et al., 2018). The long-term objective of the EU policies is to reverse this trend through a series of waste management principles and practices. The prevention and reuse of waste generated through changes in consumers' behavior and industrial production remain on the top of the actions that are recommended by the EU waste management hierarchy.

Recycling constitutes the next crucial step to face this alarming tendency on waste generation. Indeed, the revised Waste Framework Directive of 2008 (Directive 2008/98/EC) has actively promoted the application of waste recycling biotechnologies with the final aim at transforming Europe into a "recycling-based society" that conceives solid waste as potential resources and drivers of the local economy. Notably, composting and anaerobic digestion are one of the most recommended approaches to valorize the organic matter contained into solid wastes and residual organic products (ROP), enabling to convert them into high value-added products such as soils amendments, fertilizers, and energy. Other conversion bio-technologies can be also implemented to produce alcohol biofuels (ethanol, methanol, etc.) and other valued-added compounds from waste biomass.

The importance of composting and methanization as waste recycling technologies is reflected in the number of treatment facilities installed and the amount of waste processed by these means. According to the European Compost Network, about 30 Mt (millions of tons) of collected biowaste are composted or anaerobically digested per year in 3500 plants across Europe, which represent only 30% of the annually generated biowaste. The EU set an ambitious goal of extending this quantity of biowaste recycled up to 65% by 2020 (Siebert, 2015). In France, The Environment & Energy Management Agency (ADEME) reported the existence of 820 composting facilities in 2007, from which 100 installations were devoted to manure stabilization. According to this inspection, a total 6 Mt of waste were processed, and 2 Mt of compost were produced per year by 551 of the surveyed plants (ADEME, 2007). These numbers were presumably larger since they did not take into account the amount of waste treated by the not-inspected plants (269) and the application of local waste management strategies (i.e., home composting) accounting for the treatment of 0.6 Mt of food waste and 4.5-5 Mt of green waste (ADEME, 2018). Recently, Le Club Biogaz (2018) estimated the presence of 553 methanization plants in France, besides those installations functioning in wastewater treatment plants (WWTP, +76) and storage facilities of non-hazardous waste (+156). To January 2017, 227 on-farm anaerobic digestion units were established in France. The plan Energie Méthanisation Autonomie Azote (EMAA) has set a target of 1000 on-farm biogas units by 2020 (ADEME, 2017).

Although composting is considered an eco-friendly technology that plays a pivotal role in resources recovery, it is also an industrial activity which is regulated in diverse aspects. Compost quality is strictly controlled and regulated to warrant the production and use of a final safe product complying with the current standards (NF U 44051, NF U 44095, and NF U 42001). Also, regulatory frameworks are established to survey and restrict the operational composting activity, particularly to limit the release of hazardous and odorous gas emissions. Air pollution is the most relevant problem facing the composting industry because it can contribute to aggravate the greenhouse effect (methane and nitrous oxide emissions), the acidification and eutrophication of ecosystems, the augmentation of nanoparticles in the atmosphere (in the case of ammonia and hydrogen sulfide), and principally the rise of odor annoyances. Undoubtedly, odor nuisance is the air pollution repercussion or impact more easily perceived by residents living nearby waste treatment units and the one affecting principally their life quality in the short-term. Similarly, plant worker's health and welfare are negatively impacted by odors and volatile compounds emitted at the indoor areas of waste treatment units (i.e., ammonia, volatile organic compounds, H_2S) (Chollot et al., 2018).

Despite the strict regulations given by the law (decree of the 27/07/12), "More than half of the composting facilities are affected by odor problems" which means roughly that "two-thirds of the processed wastes" are involved in odor nuisances generation (ADEME, 2007). Specifically, odor complaints are the most frequent cause of legal lawsuits between managers and neighboring residents from waste treatment units. Such conflicts have led to the temporary or even permanent closure of several sites, but also represent one of the main impediments to construct new composting plants (Schlegelmilch, et al., 2005; Tsai, et al., 2008).

In 2005 and 2012, the ADEME highlighted the lack of knowledge of odor emissions released by biological waste treatment units. This limitation on odor and chemical emissions inventories is partially attributed to the complexity of odor monitoring, which comprises the characterization of the odor-causing chemical compounds (odorants) and evaluation of the odor impact of the gas emissions (gas mixtures) by sensory methods. Odor gas emissions characterization is, however, the first step and foundation to search for and design proper odor control strategies at the waste processing sites.

The research work described in this manuscript has two-fold objectives: i) to fill the gaps of knowledge in odor and odorant characterization during the composting process of solid wastes and digestates, and ii) to broaden the understanding of the relationship between the chemical composition of gas emissions and odors.

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Chapter 1: State of the art

1. Issues arising from odor emissions during biological treatment of solid waste and residual organic products (ROP)

Olfactory and noise nuisances are responsible for a large part of complaints brought against waste processing units. In France, the ADEME (2007) underlined that 66% of the amount of organic waste treated through composting were linked to odor annoyances that caused the resistance and rejection of surrounding communities to this industrial activity. Likewise, Matias et al. (2012) informed that 54% of the complaints made by local associations opposing to waste treatment activities in France was related to odor episodes, followed by noise nuisances (31%). Odor complaints are indeed the most frequent cause of legal lawsuits between managers of waste treatment units and nearby residents. These conflicts have led to the temporary or even permanent closure of several sites, but also represent one of the main impediments to construct new composting plants (Schlegelmilch et al., 2005; Tsai et al., 2008). For instance, Praznoczy et al. (2016) evaluated the impact of waste treatment operations on health and life conditions of neighbors from four different facilities located in France. According to this study, one-third of the inspected subjects were principally annoyed by odor problems. One of the surveyed sites was a composting plant that presented a record of 102 odor complaints in 2013. As a result of the constant public pressure exerted by the local associations, this composting site was subjected to a legal procedure in 2016 to establish whether it could continue operating or not.

In addition, plant workers are repeatedly exposed to odors, hazardous volatile compounds, and bio-aerosols (microbial particles and organic dust) commonly present at high concentrations in enclosed indoor areas of the waste treatment facilities (Schlegelmilch et al., 2005). Volatile compounds and bio-aerosols cause different adverse effects on composting workers' health such as mucosal irritations and renal, hematological, neurological, hepatic alterations. Similarly, odor exposure can provoke nausea, hypersensitivity reactions, and alterations in the respiratory system (Colón et al., 2017). The exposure risk to these chemical and biological emissions can be partially attenuated through the use of ventilation systems and personal protection devices. Although the use of filter mask and respirators are highly effective against bio-aerosol emissions, it is known that these devices do not protect workers for volatile organic compounds (VOC) and odorous compounds emissions, and are seldom worn in practice (Müller et al., 2004).

In general, most of the volatile compounds released during the composting process have odor detection threshold (ODT) which are far lower than their toxic thresholds values, meaning that odors can provide a warning alert for exposure to certain compounds without implying a direct health impact (Rosenfeld et al., 2007). Aatamila et al. (2011) demonstrated that odor annoyances were directly associated with physical symptoms among residents living nearby waste treatment centers. The reported symptoms were shortness of breath, eye irritation, hoarseness/dry throat, toothache, unusual tiredness, fever/shivering, joint pain, and muscular pain. In this research work, the chemical concentrations of air

pollutant in the residential areas (1.5-3 km far from the waste treatment units) were extremely low to cause symptoms through immune-toxicological mechanisms. Instead, the authors indicated that other psychosocial reactions and pathophysiological mechanism were involved in the generation of the perceived symptoms such as individual susceptibility to odors, reduction of respiratory capacity by avoidance, stress, somatization, and environmental worry. Odor annoyances have also been related to other psychological effects such as mood disorders, anxiety, sleep disorders, a diminution of the intellectual ability, which may also be the source of other health problems (Sucker et al., 2008b).

Likewise, odors can negatively impact the economic and social activities of communities exposed to them. The neighbors of waste treatment centers who are daily confronted with odor annoyances are forced to stay in their residences, thus interfering with the full enjoyment of their properties. Social events are similarly avoided to prevent guests from experiencing unexpected malodor episodes. Furthermore, properties lying next to waste treatment units are stigmatized by the occurrence of odor plumes and environmental pollution, leading to an economical devaluation of the real estate value of those goods. Economic activities such as tourism and food business can also be drastically affected by the presence of odor nuisances, reflected into a negative perception of customers and reduction of the generated income (Schiavon et al., 2017; Praznoczy et al., 2016).

2. Odor sensory properties and odorants: mesurements and correlation

According to the norm NF EN 13725 (AFNOR, 2003), an odor is an organoleptic attribute perceivable through the olfactory sense organs while inhaling volatile odorous compounds. The major sensory dimensions or properties used to describe and characterize odors are detectability, intensity, quality, and hedonic tone. These odor dimensions are typically measured through sensory methods in which human perception and appraisal to gas samples are tested. The types of odor properties evaluated depend on the context and final aim of the odor assessments. It should also be noticed that odor-causing compounds and their concentrations are key drivers for odor perception. Therefore, odorants characterization through analytical methods constitutes a crucial element for odor monitoring and abatement.

2.1. Measurement of odor sensory properties

2.1.1. Odor concentration (OC) and detectability

The odor concentration (OC) measurement reflects the human detection or perception threshold (detectability) to a gas sample comprising one or several compounds. OC is measured through dynamic olfactometry by following the standardized NF EN 13725 guidelines. In this method, the gas sample is

diluted in series with neutral gas (ascending concentration order) and presented to a group of selected assessors to determine the dilution factor at 50 % detection threshold (Z_{50}). For standard olfactometry conditions, OC is numerally equal to Z_{50} and expressed in European odor units per cubic meter [$OU_E\ m^{-3}$] (Eq.1) (Brattoli et al., 2011). Nowadays, OC measurement is conducted through dynamic olfactometers, enabling to dilute the gas samples accurately by mixing two known flows of neutral and polluted air at different ratios thanks to mass flow controllers. To achieve standard conditions, odor panelists must be selected according to their odor sensitivity to a gas reference (n-butanol) and other specific criteria (i.e., nonsmokers and non-pregnant women).

$$OC\ (OU_E m^{-3}) = Z_{50}(\text{dimensionless}) * 1\ OU_E m^{-3} \quad \text{Eq.1}$$

When considering a gas sample containing only one odor-causing compound, the dilution factor at 50% of the detection threshold is equal to the ratio between the chemical concentration (CC in i.e., mg m^{-3}) and the odor detection threshold (ODT in mg m^{-3}). In theory, this term is also known as the odor activity value (OAV, dimensionless) and quantifies how many times the measured substance concentration overpass its reported odor detection limit as shown in Eq. 2.

$$Z_{50} = \frac{CC}{ODT} = OAV \quad \text{Eq.2}$$

For the particular case, in which just one compound is present in the gas sample (Fig. 1), OC varies linearly as a function of the odorant chemical concentration, according to the following equation (Eq.3):

$$OC\ (OU_E\ m^{-3}) = \frac{CC}{ODT} * 1\ OU_E\ m^{-3} \quad \text{Eq.3}$$

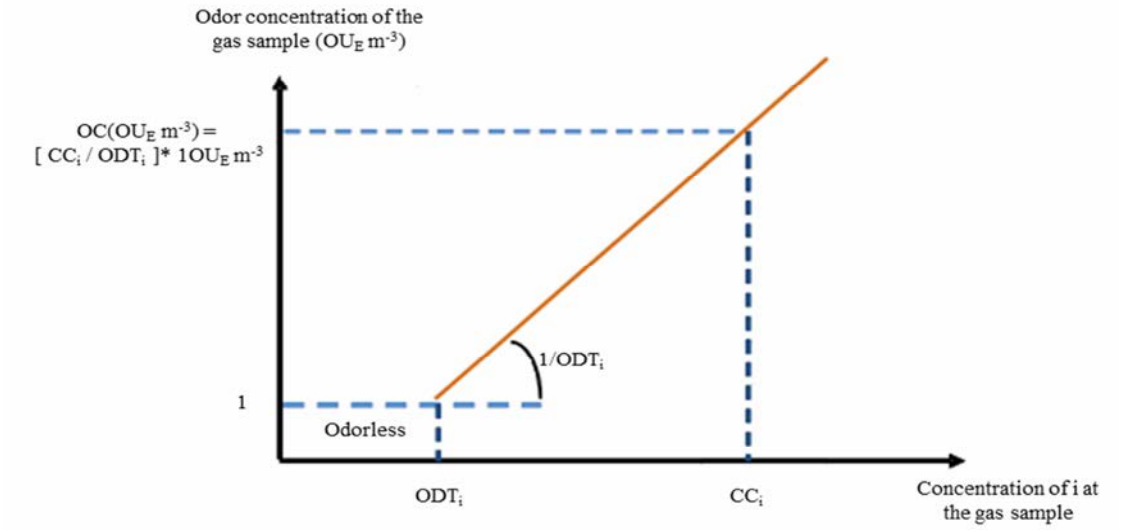


Fig. 1. Odor concentration (OC in $OU_E\ m^{-3}$) as a function the odorant's concentration for a gas sample containing one single compound (Adapted from Blazy, 2014)

Van Gemert (2011) compiled the ODT for several hundred compounds in air, water, and other media. However, the ODT values reported on literature are highly variable, even reaching some order of magnitudes of difference (Parker et al., 2012). Some of the principal causes for this variability are the differences in the olfactometric methods employed to assess them. Specifically, two principal methods have been used to determine ODT: dynamic olfactometry and triangle bag method (static method) (Ueno et al., 2009). These methods exhibit clear differences regarding their odor panel selection criteria, type of dilution presentation (ascending or descending concentration order) and way to compute Z_{50} (Rincón et al., 2019).

Moreover, and despite being selected according to their sensibility to n-butanol, human assessors can show different odor detectability responses to specific molecules as a function of their lifestyle habits and sensitivity toward tested odorants (Hansen et al., 2012; Wu et al., 2017). Some authors have proposed to compute the geometric mean of the most recent ODT values, evaluated by similar methodology, to assess OAV from complex environmental gas samples (Blazy et al., 2014; Parker et al., 2012). Rosenfeld et al. (2007) provided ODT for the main odor compounds identified in the composting emissions.

Odor concentration is often used to compute the odor emission rate (OER), defined as the product of the odor concentration ($OU_E\ m^{-3}$) and the outward flow ($m^3\ h^{-1}$) for an emitting odor source (area or point source). OER is therefore expressed in OU_E per unit time ($OU_E\ h^{-1}$, $OU_E\ s^{-1}$, etc.). Determining OER for odor generating processes provides overall insight into their environmental odor impact and constitutes important input data to design atmospheric dispersion models that are applied to predict OC for nearby receptors of odor sources (Laor et al., 2014).

2.1.2. Odor intensity (I)

Odor intensity is the perceived strength or magnitude of the odor stimulus generated by substances present in concentrations above their detection thresholds (supra-threshold olfactometry) (Brattoli et al., 2011). In general, odor intensity increases as a function of OC (Zhang, 2008). The link between odor stimuli concentration (C) and odor intensity (I) was explained by Stevens (1936) through the power function $I = C^n$, where n is Stevens' exponent which is associated with the quality of the odor stimulus and the sensory method applied to evaluate it (Köster, 1991a).

In Fig. 2, Stevens' law is applied for two gas samples containing each one a single odorant with different ODT and n. The influence of n (0.2 and 0.8) on odor intensity is presented as a function of the odor concentration (Fig. 2A and Fig. 2B). When n is low (0.2), diluting the odorous gas sample has a limited influence on the perceived odor strength, thus inferring that the odor is persistent. In contrast, when n is high (0.8), the perceived odor magnitude is proportionally affected by the OC dilution, and

thereby the odor is considered as intermittent or little persistent. For a gas sample consisting of one single compound, OC is proportional to the chemical concentration (section 2.1.1), and then odor intensity can also be expressed as a power function of the odorant's chemical concentration (CC). Hence, a linear correlation (Fig. 2C) is also observed when regressing log (I) against log (CC).

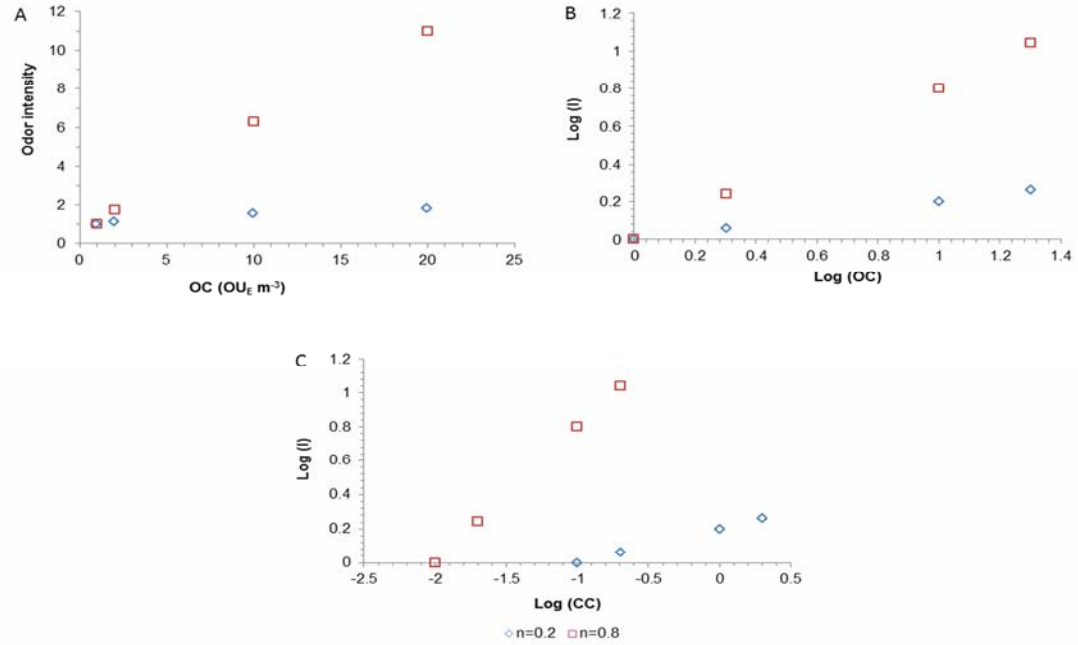


Fig. 2. Odor intensity (I) as a function of odor concentration (OC in OU_E m^{-3}) (**A**), Log (I) as a function of Log (OC) (**B**), and Log (I) as a function of Log of chemical concentration (CC) (**C**) for two gas samples containing different single compounds with *n* equal to 0.2 and 0.8

Odor intensity can be measured using different parametric methods such as descriptive category scales, magnitude estimation, and reference scales. In the category scales method, human assessors are asked to rate the odor strength according to ordinal point-scales consisting of 3-10 categories covering different odor intensities, generally going from extremely weak to extremely strong odors (Table 1). Despite the subjectivity of this method, the guideline VDI 3882 (1991, part 1) provides a detailed methodology for applying it. Another subjective approach to evaluate odor intensity is to compare the perceived magnitude of two odor sources. To conduct this odor intensity assessment, the panelists assign an arbitrary value of odor magnitude to one reference substances and then assess the intensity of a second target gas sample on the basis to first earned odor experience (Brattoli et al., 2011). Finally, the most applied methodology to evaluate odor intensity is the reference scale method which has been standardized by NF X 43-103 (AFNOR, 1996) and ASTM E544-99 (2004). In this case, odor intensity of environmental gas samples is scored by comparing and matching the odor with the perceived odor intensity of a series of concentrations of certain reference compound (i.e., n-butanol, sec-butanol, and pyridine). The range of concentrations levels used as references can be presented to the odor panelists through dynamic olfactometry (dynamic-scale) or a set of bottles with fixed dilutions of the standard in

water (static-scale). When using n-butanol as a reference compound, the concentrations scales have typically a starting point of around 10 ppm and a top concentration as high as 25 ppm.

Table 1. A nine-point scale employed to measure odor intensity through the category scale method

Appraisal/Description	Evaluation
Extremely weak	1
Very weak	2
Weak	3
Mildly weak	4
Distinct	5
Mildly strong	6
Strong	7
Very strong	8
Extremely strong	9

Odor intensity measurement plays a vital role in evaluating the odor impact of odor sources and determining the efficacy of implemented odor control strategies. For instance, two odor sources presenting similar detectability (i.e., OC= 10 OU_E m^{-3}) can have a different odor nuisance potential as a result of variations on their odor intensity (strength), hedonic tone, and odor quality.

2.1.3. Odor quality (character)

The perceived olfactory quality is a description of the odors in terms of what they smell like, having as a reference previous personal experiences and a list of reference vocabulary (Leonardos, 1999). This odor dimension has been widely studied and developed in the fields of perfumery, cosmetics, and food sciences. Two principal approaches are applied to evaluate the odor quality: (i) describing the odor character based only on semantic odor descriptors/notes (i.e., fecal, sweet, earthy, etc.), and (ii) using reference compounds in order to avoid the difficulties related to vocabulary-based descriptions (Köster, 1991a).

In the literature, two methodologies have been principally employed to assess odor quality for composting gas emissions:

(i) The « Field of Odors ® » is a method initially created by Jean-Noël Jaubert and IAP-SENTIC in 1983 to characterize fragrances and perfumes, but then adapted to evaluate the odor quality of olfactory nuisances. This methodology allows positioning the odor stimulus into an organized collection of 42 reference odorants which are simultaneously grouped into 15 different odor poles or families according to their odor character (Jaubert et al., 1995).

(ii) The composting odor wheel is a classification scheme that associates the odor quality of an olfactory nuisance with the odor-causing compounds (Suffet and Rosenfeld, 2007). To link both, the odor character and chemical composition, the odor wheel relates common odor descriptors and volatile compounds identified beforehand during the composting process of solid wastes and residual organic products (Fig. 3). The main compounds used as references are odorous molecules containing sulfur, nitrogen, and oxygen atoms (Rosenfeld et al., 2007). As seen in Fig. 3, the composting odor wheel is divided into different odor qualities notes and categories. The inner circle accounts for the general odor categories and descriptors, for instance, "rancid." The outer circle highlights possible variations and specific notes found within each primary odor category (i.e., rancid/ vinegar). Finally, each odor descriptor is linked to an external list of odor-causing compounds (i.e., rancid/vinegar to acetic acid). It is worthy to mention that odor notes located at the wheel's left side are expected to be offensive (dark green area), whereas the wheel's right side is composed of substances eliciting rather a pleasant sensory experience (light green area). Rosenfeld et al. (2007) provided a comprehensive list of odor descriptors for the main compounds identified upon composting process. Suffet and Rosenfeld (2007) emphasized the need for an improvement of the odor wheel with the advancement of scientific knowledge related to odor quality.

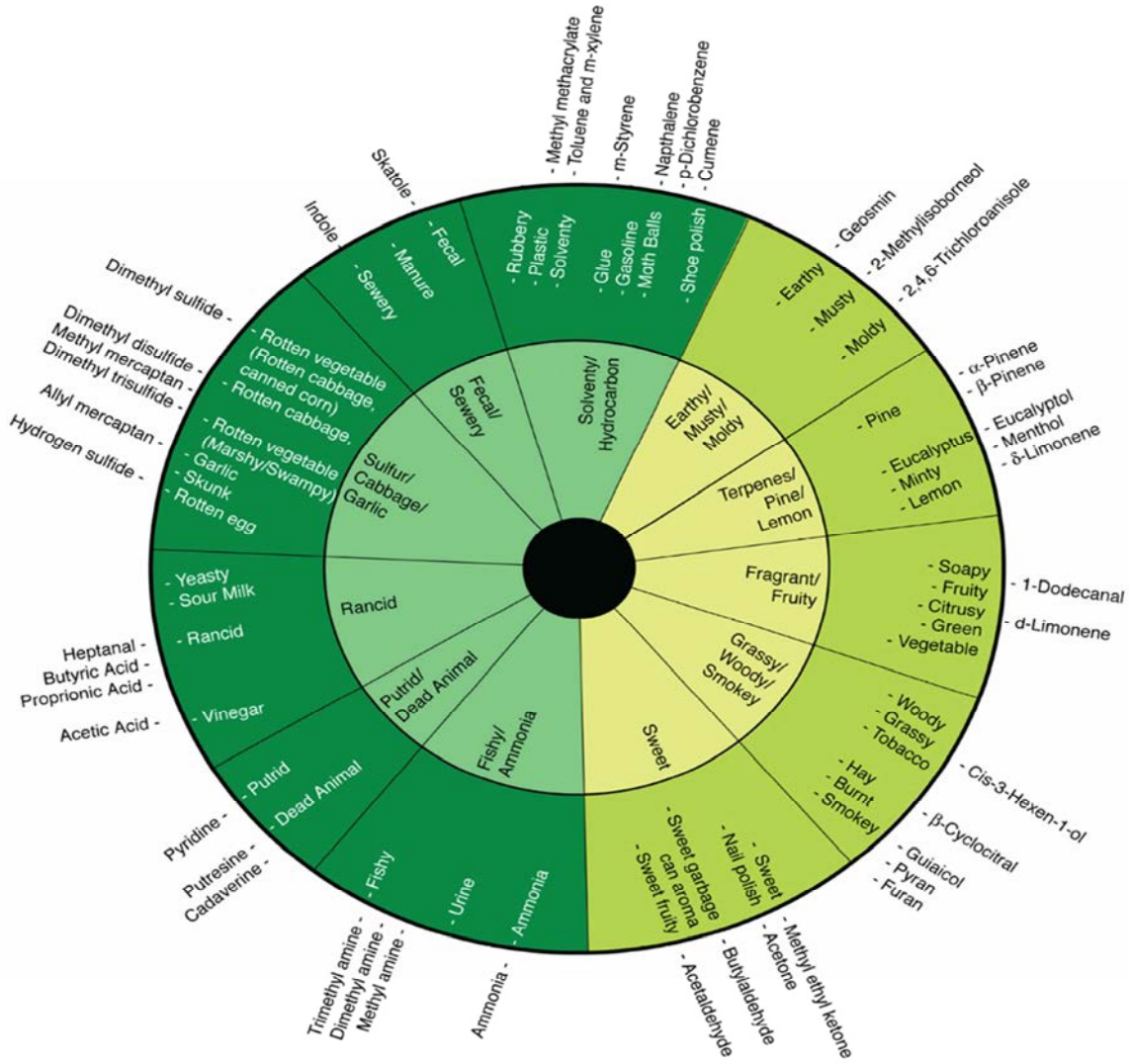


Fig. 3. Composting odor wheel (Rosenfeld et al., 2007)

2.1.4. Hedonic tone

The hedonic tone is a category judgment of the relative pleasantness and unpleasantness of the perceived odor stimuli (NF EN 13725, 2003). This category appraisal may differ widely from subject to subject as a function of their emotions and previous personal experiences and highly depends on the chemical composition, the odor concentration and intensity of the odor samples. The guideline VDI 3882 (part 2, 1994) provides a standardized methodology for evaluating this odor dimension using a nine-point category scale of judgment (Fig. 4). In this method, a group of panelists is initially selected on the basis of their sensitivity to two reference solutions (vanillin and guaiacol). Dilutions of the odor gas sample are then presented to the screened panelists at six different concentrations. The initial concentration is performed by diluting the gas sample with neutral air at 50% detection threshold. The next presentations consist of supra-threshold concentrations obtained by decreasing the dilution rate successively in a step factor of two. Panelists are required to judge the relative pleasantness or unpleasantness of every

performed dilution considering the nine-point category scale depicted in Fig. 4. The hedonic tone can be represented in a histogram describing the frequency of the responses for each assessed category and dilution (odor concentration).

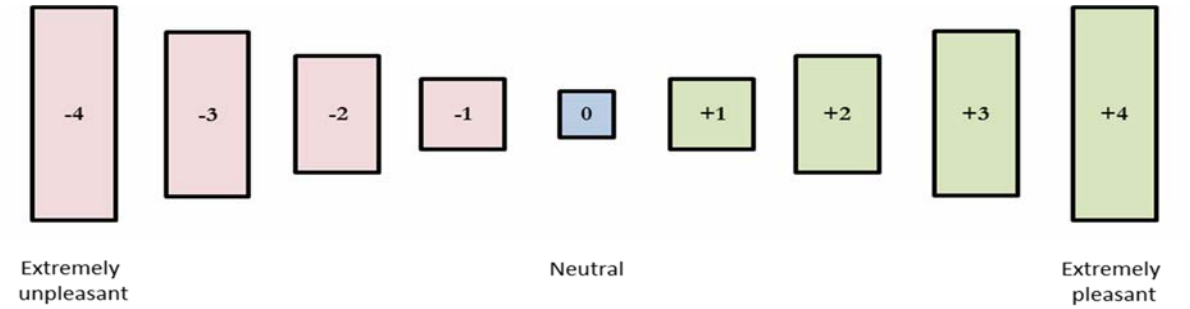


Fig. 4. Nine-point category scale to assess hedonic tone according to the VDI 3882/Part 2 guideline

The hedonic tone is a relevant odor property to describe odor nuisances because it provides a direct insight into the acceptance levels of receptors through the use of common vocabulary and language descriptors. For instance, the measurement of hedonic tone and odor intensity were found to be critical parameters while characterizing the degree of odor annoyance of residents living nearby industrial sites in Germany (Sucker et al., 2008a, 2008b).

2.2. Odor nuisances measurement

Odor nuisances are principally estimated by determining the odor concentration (detectability) at the residential areas where the odor is perceived. Odor samples collected downwind of the emitting sources are generally too diluted to conduct laboratory olfactometry (Laor et al., 2014). Hence, the most widely applied approach to determine OC at the receptors areas is to characterize the odor emitting source in terms of OC and OER, and then use this input data into atmospheric models to predict OC and simulate how odors are dispersed (Capelli et al., 2013). The accuracy of OC predictions is highly influenced by the quality of the dispersion model inputs, including the odor source characterization (flows, OER, temperature) but also meteorological, topography and land cover data (Fig. 5) (Laor et al., 2014).

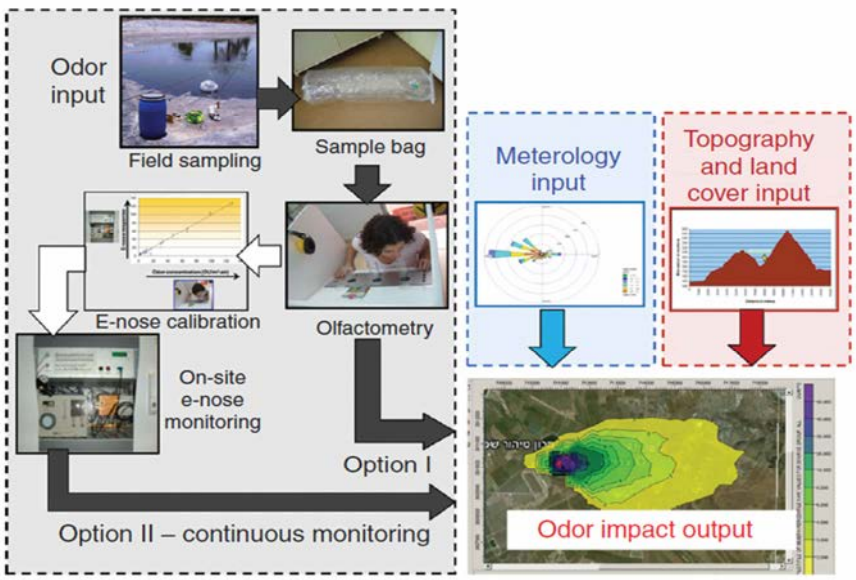


Fig. 5. Input data required to construct odor dispersion models and e-nose application on odor modeling (Laor et al., 2014)

In France, composting sites are considered as "Installations Classified for the Protection of the Environment (ICPE)." As a part of ICPE, composting facilities are regulated by the heading 2780 and subject to a series of authorization, registration, and self-declaration control systems. For composting units subject to an authorization frame, an odor dispersion model must be conducted to warrant the waste treatment plant compliance with the established regulations. In this case, the OC predicted through the dispersion study must not exceed 5 OU_E m^{-3} for more than 175 hours per year (2% of exposure per year) for residential areas located within a distance of 3000 m from the composting plant boundaries (decree of 22/07/08, amended by the decree of 27/07/12).

The United Kingdom Environmental Agency (UK Agency, 2002) set OC limits at 2% of annual exposure time (within a distance of 3000 m) based on the hedonic tone of different odor emitting activities. For instance, a threshold value of 1.5 OU_E m^{-3} was established for activities involving waste fermentation, wastewater treatment or oil refining. In contrast, the predicted OC during dispersion studies for industrial processes such as livestock farming, fat frying, sugar beet processing must not exceed 3 OU_E m^{-3}. Other less odorous industrial activities, such as chocolate manufacturing, coffee roasting, bakery, breweries, and flavor production, must not present ground OC levels superior to 6 OU_E m^{-3} (Capelli et al., 2013).

The estimation of odor annoyances based on OC evaluation has two principal drawbacks: i) OC is not a direct measurement of odor annoyances; thereby other odor dimensions such as hedonic tone and odor quality should be assessed or correlated to understand the real impact of odor plumes on receptors.

ii) OC predictions through dispersion models can be drastically affected by unexpected changes in the meteorological conditions (wind speed and direction, rain, etc.).

Another relevant approach to measuring odor annoyances in the concerned areas is to assess the odor properties described in the previous sections by well-trained panelists through field olfactometry. Field inspections have as a major gain that odor impact is directly evaluated by human subjects in the area affected by odor problems, thus providing a more realistic view and description of the generated odor nuisances than the outputs from dispersion models. Nevertheless, the use of field olfactometry is constrained by its high cost, difficult implementation, and the significant influence of environmental stressors and meteorological conditions on the acquired results (Capelli et al., 2013; Laor et al., 2014).

Undoubtedly, neighbors of waste treatments plants must also be engaged in the characterization of odor nuisances. This type of odor field monitoring can be carried out by (i) analyzing and compiling the odor complaints, (ii) conducting regular surveys to collect detailed information about odor episodes (i.e., grid field inspection), and (iii)assessing different odor properties through un-trained panels of exposed residents (Sucker et al., 2008b). The benefits and disadvantages of applying these approaches are discussed by Köster (1991 b). In the case of un-trained panel evaluation, dwellers are required to respond to a survey where they score the level of odor nuisances perceived in their quotidian life (Fig. 6). The answers obtained through this sensory evaluation can be statistically processed to obtain an odor nuisance index (ONI).

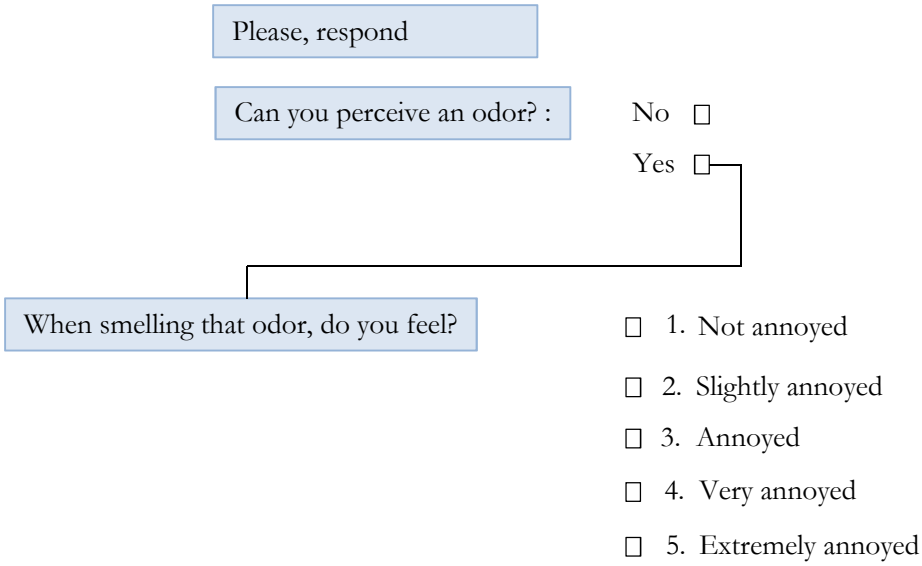


Fig. 6. Questionnaire employed to evaluate odor annoyances by an untrained odor panel of residents (Adapted from Köster, 1991b)

Finally, another promising approach to detect, estimate and quantify odors consists of the online and on-site odor monitoring through electronic noses (e-noses). E-noses are arrays of nonspecific gas sensors that react to several chemical compounds found in the examined out-gas to produce specific signal patterns. These signature profiles are then treated (by data analysis techniques) and correlated to olfactometry measurements through a training/calibration process (Fig. 5). The calibrated electronic devices are utilized to analyze continuously polluted air at the receptor or odor sources in a direct and useful manner. E-nose's outputs can be similarly added to real-time odor dispersion models with the aim at predicting OC (Laor et al., 2014). Nevertheless, the application of e-nose is still in continuous evolution because of sensors' sensitivity problems, sensors drift (slow outputs changes during monitoring), and undesired e-nose responses to meteorological conditions (temperature and moisture)(Capelli et al., 2013; Nicolas et al., 2001; Sironi et al., 2007).

2.3. Odor-causing compounds: measurements and correlation with odor properties

Odor emissions are often composed of a large cocktail of inorganic and organic volatile compounds. Nonetheless, linking odor sensory properties of a gas to its chemical composition is still a challenge.

Sensory and chemical analyses are complementary approaches to face the difficult challenge of monitoring odors in composting facilities. While sensory methods (i.e., dynamic olfactometry) offer a direct measurement of the odor impact caused by complex gas mixtures on a group of human assessors, analytical methods (i.e., GC/MS) enable to identify and quantify the odorants driving the physiological odor perception. Both methods have gains and limitations and must be employed according to each specific scenario. For instance, if the ultimate goal is to design and install odor abatement technologies in a waste treatment unit, one may principally require a full understanding of the emissions' chemical fingerprints and the odor-causing compounds. However, if the final aim is to assess odor annoyances as a response of odor complaints from residents, sensory measurements involving stakeholders must be preferentially taken into account (ADEME, 2012). Hence, there is a clear interest in coupling both methodologies to obtain more broaden knowledge about odors generation and investigate how feasible it is to predict odors based on sole instrumental-based methods. In particular, whenever it is possible, engineers and plant operators prefer to conduct chemical analysis over olfactometric analysis (Laor et al., 2014) due to the high economic investment required to perform regular sensory measurements (need of a representative human panel and extensive sampling campaigns), and the inherent bias and subjectivity of human response when assessing odor nuisances (Hansen et al., 2016; Wu et al., 2017).

2.3.1. Determination of the chemical composition

A broad range of instrumental-based techniques has been developed to face the complex challenge of odorant identification and quantification. The most common approaches are gas chromatography (GC) coupled with the diverse type of detectors, colorimetric reaction-based essays (gas tube detectors), and wet chemical methods.

Colorimetric tube detectors are a cheap and quick methodology to analyze online compounds such NH_3, volatile sulfur compounds (VSC), and amines (Mao et al., 2006; Tsai et al., 2008). However, this technique is only useful for chemical identification and preventive monitoring because of its large error range of measurement and low detection limits.

The wet chemical method is based on the absorption phenomena of air pollutants while passing through a measured volume of chemical solutions set on series (gas traps or scrubbing). This method is typically employed for quantifying in continuous ammonia, VSC, aldehydes, and amines (Zhang, 2008).

Gas chromatography is regarded as the most precise and robust analytical technique to separate, identify and quantify VOC and VSC (Font et al., 2011). In this method, complex mixtures of volatile compounds are carried by a mobile phase (i.e., N_2 and He) toward a column coated with a stationary phase where analytes are eluted and separated according to their chemical affinity and interactions with the solid phase surface. Once separated, volatile compounds are identified through mass spectrometry (GC/MS) or other detectors (i.e., electrochemical detector), enabling to determine VOC and VSC even at trace level concentrations (Muñoz et al., 2010). Despite its high chemical sensitivity (detection limits: 10-100 pg), GC/MS is generally coupled to some pre-concentration techniques such as solid phase microextraction (SPME) and thermal desorption tubes (TD-GC/MS). Since certain odorants can be present at extremely low concentrations in the ambient air, these pre-concentration stage is necessary to reach a suitable amount of analytes that can be possibly resolved by the GC/MS (Font et al., 2011; Laor et al., 2014). Finally, hybrid technology combining both, sensory and chemical methods, such as GC/MS equipped with a sniffing port (GC/MS-O) have shown good performances on elucidating hundreds of odorants from odor samples and recognizing the different odor characters of separated compound (J. Barczak et al., 2018; Fisher et al., 2018).

2.3.2. Correlation between chemical composition and odor concentration

A first straightforward strategy to correlate sensory measurement with analytical methods consists of using the chemical composition of volatile compounds and their concentration levels as predictors. Indeed, univariate and multivariate models based on chemical concentrations have been successfully

employed to predict OC for composting gas exhaust. Defoer et al. (2002) found a close correlation between OC and total VOC concentrations (R^2=0.97), as well as with ester and ketones concentrations (R^2=0.9). Noble et al. (2001) indicated that H_2S and DMS concentrations could accurately explain 96% ($p<0.001$) of the OC variability when they were regressed in a multiple linear regression (MLR) model. Hanajima et al. (2010) demonstrated that OC was well correlated to DMS, methanethiol and ammonia concentrations (R^2= 0.7) during the aerobic treatment of swine feces. Lately, VOC and H_2S concentrations have been similarly used as input data to develop OC prediction models during composting of MSW at industrial scale (Colón et al., 2017; Gutiérrez et al., 2015a) with high R^2 fluctuating from 0.97 to 0.98. Some efforts have been similarly devoted to predicting odor intensity of gas emissions produced while storing animal manure with fairly good results (R^2=0.87) (Zahn et al., 2001). Nevertheless, predicting odors by considering only chemical concentrations must be taken with care since compounds in the gas mixtures can contribute to a different extent to the odor stimuli depending on their odor detection thresholds (ODT) and the chemical and physiological interactions (Kim and Park, 2008). For instance, certain compounds with high ODT such as acetone ammonia, and esters can be well correlated to OC without exerting a substantial impact on odor perception, meaning that they just follow a similar emission pattern than OC (Defoer et al., 2002; Hansen et al., 2016; Parker et al., 2012).

A second approach is to construct odor prediction models based on the odorous potential of the substances comprising the gas mixtures through the calculation of OAV. As explained in section 2.1.1, OAV is an analogous term to odor concentration defined as the ratio of a compound's chemical concentration to its corresponding ODT. Here, two main odor surrogates derived from OAV calculation have been employed to develop simple linear regression models to predict OC:

i) the sum of OAV (OAV_{sum}) from all substances detected in the odorous gas sample in which odor perception is assumed to be the result of the additive contribution of every single component (Capelli et al., 2008; Parker et al., 2012; Wu et al., 2017).
ii) the maximum OAV (OAV_{max}) that represents the molecule exhibiting the largest OAV, and then likely the most significant odor contributor (Blazy et al., 2015; Kim and Kim, 2014).

Some authors have concluded that OAV is a better OC predictor than the compound's chemical concentration. For odorous gas samples collected in industrial sites, the correlation attained between OAV_{sum} and OC was considerably higher than the one observed between OC and total VOC concentration (R^2= 0.84 and 0.4, respectively) (Capelli et al., 2012). Similarly, Kim and Park (2008) determined that OC variability could be better explained through OAV_{sum} (87%) than the total VOC content (67%). A very week correlation (R^2= 0.4) was also encountered when comparing OC and the total VOC concentration on the working face of a landfill (Wenjing et al., 2015).

Although OAV_{max} are well regressed against OC, this odor surrogate can underestimate the measured OC in some orders of magnitude (Capelli et al., 2013; Wu et al., 2017). In an attempt to solve this discrepancy, Wu et al. (2017) proposed to use a scaling factor (k) without obtaining a clear improvement. Three principal shortcomings hinder the use of OAV_{max} and OAV_{sum} on OC prediction. The first drawback is associated with the considerable variation on ODT values reported in datasets as a result of the differences on sensory methods and panel selection criteria during their measurements (i.e. dynamic olfactometry vs. triangle bag method), as well as the variability of human panel responses (Hansen et al., 2016; Rincón et al., 2019; Wu et al., 2017). Secondly, the odorous potential for certain substances is unknown because their ODT are not reported in the current literature. Finally, the OAV approach does not consider the occurrence of possible interactions among molecules during odor perception which may be responsible for synergistic, antagonistic, and even neutralizing effects (Muñoz et al., 2010; Wu et al., 2015).

Parker et al. (2012) developed MLR models to predict OC based on OAV of the main odor-causing compounds present in the exhaust airstream of animal facilities. According to this study, 10-parameter MLR models had better predictability performances (R^2= 0.66-1) than OAV_{max} (0.2-0.5) and showed less underestimation of the conducted sensory measurements. In contrast to OAV_{sum}, the multivariate models were expected to provide different weights to the compounds present in the odor mixtures, thus likely representing the possible odorant interactions occurring in the gas samples. Generally, multivariate analyses seeking to predict OC or other odor attributes through OAV have been widely explored in food sciences (Campo et al., 2005; Lee and Noble, 2003; Vilanova et al., 2012); however, for environmental odor pollution, the research work of Parker et al. (2012) was pioneer.

For composting odor emissions, the link between OAV and OC has been barely addressed in the literature. Blazy et al. (2015) found that OAV_{max} and OAV_{sum} were well regressed against OC (R^2> 0.87) when aerobically treating pig slaughterhouse sludge. Nevertheless, since odor emissions in composting can largely vary according to the waste nature, it is thus necessary to validate the feasibility of this odor surrogates as OC predictors during the treatment of different organic substrate. Notably, the use of powerful multivariate techniques such as partial least square (PLS) regressions must be explored as they could provide a more extensive understanding of the relationships between OAV and OC. PLS regression is a multivariate technique typically used in sensory sciences which prevents MLR's problems such as variables collinearity (Aishima, 2004). Lastly, the measurement of ODT under standardized conditions (EN 13725) is crucial to strengthen the application of the OAV approach on odor assessments, and eventually reach a consensus on the published ODT values.

Odor concentration is typically employed by the regulatory framework (decree of 27/07/12) to determine odor nuisances, which explains the great interest in correlating this sensory property to the chemical composition of the odor mixtures. However, OC does not take into account other important

odor dimensions also governing the odor nuisance perception, namely, odor quality and hedonic tone. Hence, the correlation between OC and chemical composition could be then related to other odor sensory properties in order to obtain a wider insight into odor nuisance measurement.

3. From organic wastes to odor nuisances

3.1. ICPE regulations regarding odor emissions from composting process

Composting facilities are considered as "Classified Installations for the Protection of the Environment" (ICPE) and are subject to an authorization, registration, and declaration control system, described at the heading 2780. The decree of 22/04/08 amended by the decree of 27/07/12 lays downs a list of technical requirements and regulatory notions for composting installations under an authorization frame. Concerning odor regulatory measures, this directive establishes a minimum setback distance of 200 m for setting composting plants, which may be reduced up to 50 m for enclosed facilities equipped with gas treatment units. Plant managers and operators are required to follow specific instructions during the design, construction, and operation of the composting facilities in order to limit odor nuisances. Chemical and dust emissions should be preferentially extracted and captured at the emitting source to be then conveyed toward air treatment systems. The final gas streams being released into the atmosphere must be regularly monitored under standardized conditions and contain less than 5 mg Nm^{-3} of H_2S for a mass flow rate superior to 50 g h^{-1} and 50 mg Nm^{-3} of NH_3 for a mass flow rate above 100 g h^{-1}.

For new facilities, odor impact assessments describing the type of odor emitting sources present in the process (punctual or continuous) and their flow rates must be conducted and presented in order to apply for an operating license. Additionally, an odor dispersion study must be performed by considering the local topographic and meteorological conditions to determine if predicted OC does not exceed the established regulatory limits. Accordingly, the surrounding areas of the composting plant within a radius of 3000 m must not exhibit an OC superior to 5 OU_E m^{-3} for more than 175 hours per year (2% of exposure per year). In the case of already running composting facilities, odor dispersion studies are not necessary if the measured odor emissions rates (OER) are below than $20 \cdot 10^6$ OU_E h^{-1} and there are not odor complaints from neighbors.

3.2. Solid waste and residual organic products (ROP)

Solid waste and ROP can be classified according to the type of anthropogenic activities involved in their generation, and the process used throughout their collection and valorization. Hence, three principal waste sources are identified: municipal, industrial, and agricultural wastes. The annual generation of the different type of solid waste and ROP in France is summarized in Table 2.

Municipal solid wastes (food waste, paper, cardboard, sanitary textiles, green wastes) are principally collected door-to-door, either being mixed with non-biodegradable products (plastics, metals, non-recyclable products) or separated through biowaste selective collection. A significant part of this organic fraction of municipal solid wastes (OFMSW) is managed locally by stakeholders through home composting (5.1 Mt). Additionally, municipalities are also responsible for collecting and treating another type of organic matrices such as sewage sludge, green wastes, and food waste from restaurants, food trade, and markets. Notably, these formers substrates (food waste) are also considered as bio-waste. Most of the organic waste generated by industrial activities is derived from the agri-food industries (AFI) (Table 2). It is worth mentioning that agricultural activities constitute the principal waste generation source by accounting for a net annual waste production of 250 Mt.

Table 2. Annual generation of solid wastes and ROP in France (Adapted from de Guardia and Blazy, 2018)

Waste source	Type of waste	Annual generation (Million tons per year)
Municipal solid wastes (MSW) and other wastes treated by municipalities	Collected by public service (MSW):	
	Food waste	7.1
	Paper, cardboard, sanitary textiles	7.2
	Green wastes	5.9
	Local waste management (i.e., home composting)	5.1
	Sewage sludge	9
	Green waste (neighborhoods and business)	4.2
	Food waste from restaurants	1.1
	Other food trade business	0.8
	Markets	0.4
Industrial wastes	Agri-food industries (AFI):	
	Sludge and effluents	26
	Organic wastes	4
	Paper mill (sludge and woody residues)	1
	Others	0.8
Agricultural wastes	Livestock effluents (manure, slurries)	120
	Crop residues and silviculture	130

In particular, these organic substrates can be distinguished in terms of their physicochemical and biological characteristics (i.e., moisture, biodegradability, pathogenic microorganism content, etc.), the amount of waste to be managed (going from a few kilograms to several tens of tons) and their generation context (i.e., households, public service, commercial, industrial or agricultural activities in urban or rural areas).

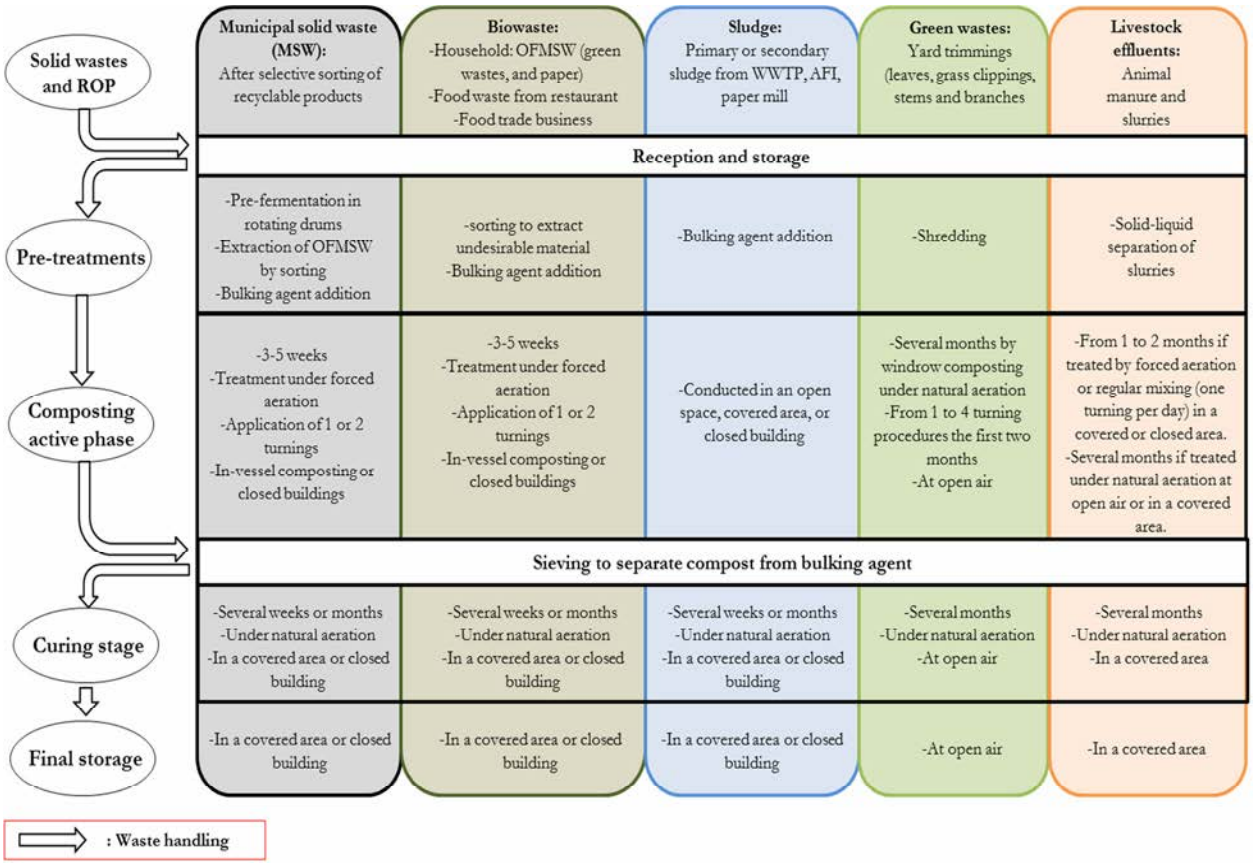
The continuous expansion and development of anaerobic digestion to valorize and treat household waste, biowaste and livestock effluents have been accompanied by the generation of a new waste material called anaerobically digested substrates or digestates. The sale or placing on the market of digestates is conditional to their post-treatment through composting process with the aim at stabilizing their remaining

organic matter content, removing possible harmful microorganism, and controlling hazardous and odorous gas emissions before spreading (i.e., H_2S and NH_3) (Rincón et al., 2019; Zeng et al., 2016). In the agricultural sector, the low biodegradability of livestock effluents has led to methanizing them together with other substrates such as AFI wastes.

3.3. Biological treatment processes of organic wastes and odor emissions

3.3.1. Process stages and operations

Composting (aerobic treatment) and methanization (anaerobic treatment) are the main biological treatments used to valorize organic wastes and ROP. Biological processes under anoxic conditions (alcoholic fermentation) are less widespread. The main operational stages and steps involved in the composting and methanization process of some key solid waste and ROP are summarized in Fig. 7 and Fig. 8, respectively.



	Municipal solid waste (MSW): After selective sorting of recyclable products	Biowaste: -Household: OFMSW (green wastes, and paper) -Food waste from restaurant -Food trade business	Sludge: Primary or secondary sludge from WWTP, AFI, paper mill	Green wastes: Yard trimmings (leaves, grass clippings, stems and branches	Livestock effluents: Animal manure and slurries
	Reception and storage				
Pre-treatments	-Pre-fermentation in rotating drums -Extraction of OFMSW by sorting -Bulking agent addition	-sorting to extract undesirable material -Bulking agent addition	-Bulking agent addition	-Shredding	-Solid-liquid separation of slurries
Composting active phase	-3-5 weeks -Treatment under forced aeration -Application of 1 or 2 turnings -In-vessel composting or closed buildings	-3-5 weeks -Treatment under forced aeration -Application of 1 or 2 turnings -In-vessel composting or closed buildings	-Conducted in an open space, covered area, or closed building	-Several months by windrow composting under natural aeration -From 1 to 4 turning procedures the first two months -At open air	-From 1 to 2 months if treated by forced aeration or regular mixing (one turning per day) in a covered or closed area. -Several months if treated under natural aeration at open air or in a covered area.
	Sieving to separate compost from bulking agent				
Curing stage	-Several weeks or months -Under natural aeration -In a covered area or closed building	-Several weeks or months -Under natural aeration -In a covered area or closed building	-Several weeks or months -Under natural aeration -In a covered area or closed building	-Several months -Under natural aeration -At open air	-Several months -Under natural aeration -In a covered area
Final storage	-In a covered area or closed building	-In a covered area or closed building	-In a covered area or closed building	-At open air	-In a covered area

Fig. 7. Summary of operational stages involved in the composting process of solid wastes and ROP

Composting process enables the bio-stabilization of organic matter contained in solid wastes and ROP under controlled aerobic conditions. To reach the material stabilization, organic matrices are

aerobically decomposed by microorganisms that use them as sources of energy and nutrients to fulfill their metabolic needs. The aerobic treatment of solid wastes comprises a first stage called the active phase where most of the readily biodegradable organic matter is consumed, followed by a curing stage involving the reorganization of residual organic matter to produce a humus-like product (compost). During the active phase, heat is produced as a result of the microbial oxidation of organic matter, favoring the substrates' drying and sanitization. Also, the compostable substrates can be regularly mixed (turning process) to keep aerobic conditions in the composting piles along the active phase. The compost obtained through this biological process must comply with amendment standards (NF U 44051, NF U 44095, and NF U 42001) to warrant the safety and quality of the final product.

Contrarily, methanization is based on the anaerobic stabilization of organic substrates to generate two principal products: methane and digestates. To be employed as fertilizers or soil amendments, digestates must be composted or followed a homologation process to validate their final quality and safety. If these regulatory conditions are not met, anaerobically digested substrates retain their status of solid wastes, thus being disposed in landfills or subject to spreading plans. In fact, anaerobic digestion systems often include, but not always, a composting stage (active phase and/or maturation). When exhibiting high moisture contents, digestates can also be pre-treated through a solid-liquid separation before being composted.

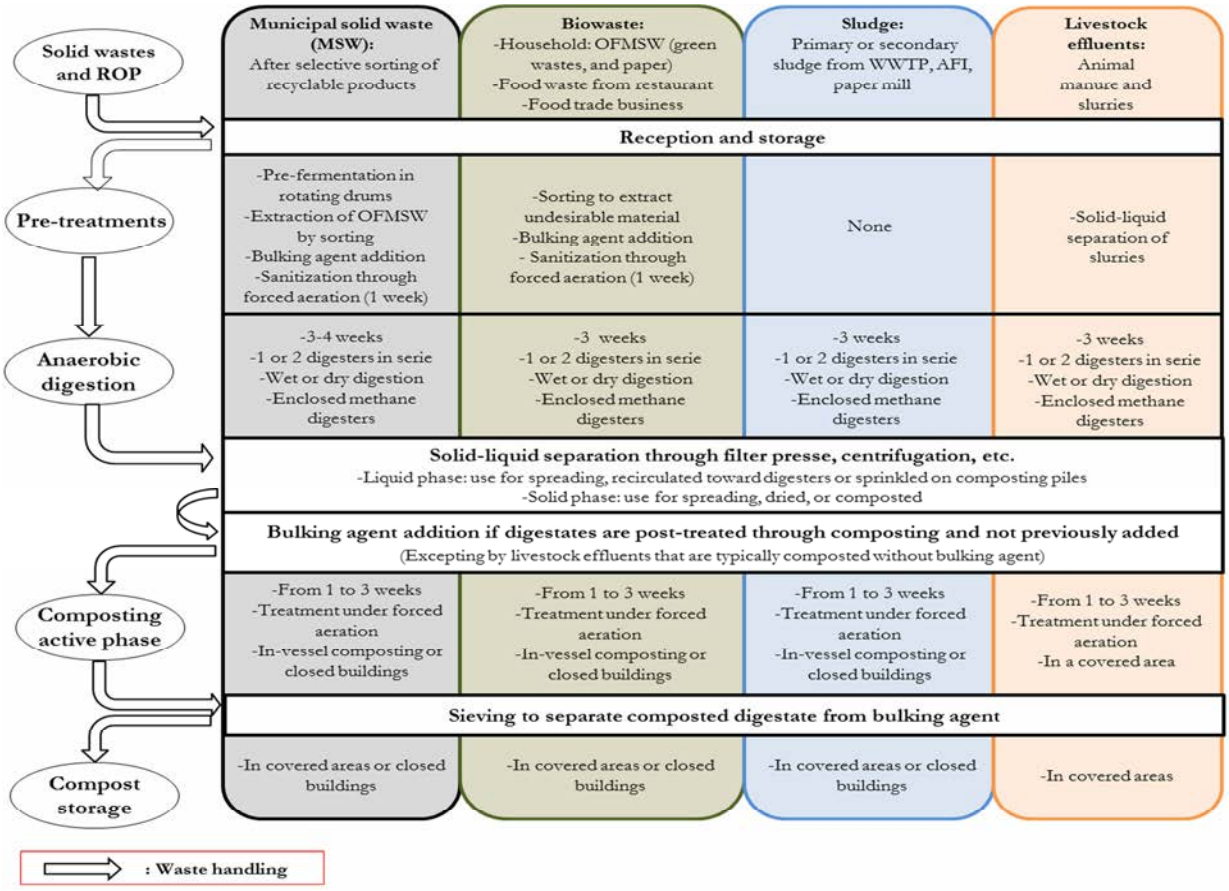


Fig. 8. Summary of operational stages involved in the methanization process of solid wastes and ROP

In general, composting and methanization have for common the following operational stages (Fig. 7 and Fig. 8):

i) The reception and storage of inputs.
ii) Pre-treatments preceding the active phase or anaerobic digestion, depending on the solid waste and ROP nature or the type of methanization (i.e., dry or wet anaerobic digestion) and composting process (i.e., window, in-vessel composting) conducted.
iii) Post-treatment such as sieving aiming at separating the compost from the bulking agent.
iv) The final storage of digestates and composts.
v) Waste handling along every operational step of the process.

3.3.2. Mechanisms and conditions favoring odorous compounds emissions

De Guardia and Blazy (2018) provided an inventory of the main odorous compounds emitted during composting, their formation mechanisms and odor properties (Table 3). Most of the compounds responsible for malodors during composting (hydrogen sulfide, thiols, alkyle sulfides and volatile fatty acids) have low odor detection threshold value or/and low henry's constant and they are produced under anoxic or anaerobic conditions meaning the chemical composition and odor potential of gas emissions released along the biological treatment of solid waste and ROP are strongly influenced by the physicochemical and biological characteristics of the treated organic matrices, as well as by the gaseous exchanges occurring between the substrates and the gas interphase.

Table 3. Formation mechanism and odor properties of volatile compounds released upon composting of solid wastes and ROP (adapted from de Guardia and Blazy (2018))

Chemical family	Formation mechanism	Chemical substance	Odor descriptors	Henry constant ($M\ atm^{-1}$)[a]	ODT ($\mu g\ m^{-3}$)[b]	Principal waste sources
Inorganic nitrogen-containing compound	-Amino acid deamination, hydrolysis of urea under aerobic or anaerobic conditions	-Ammonia	-Ammonia/ piquant	50	1450	Sewage sludge, livestock effluents, yard trimmings, municipal solid waste (MSW), organic fraction of MSW (OFMSW), and digestates
Inorganic sulfur-containing compound	-Sulfate reduction under anoxic conditions (lower reduction in the presence of NO_3^{-1}) -Reduction of organic sulfur compounds under anaerobic conditions	-Hydrogen sulfide	-Rotten eggs	0.1	0.5	All solid wastes and ROP, except by lignocellulosic material
Thiols (RSH)	-Anaerobic degradation of proteins built by sulfur-containing amino acids -Methylation of H_2S -Reduction of alkyl sulfides	-Methanethiol -Ethanethiol[c]	-Rotten cabbage -Rotten egg, garlic, onion[c]	0.45 0.34	0.14 0.02	All solid wastes and ROP, except by lignocellulosic material
Alkyl sulfides (RSR and RSSR)	-Anaerobic of proteins built by sulfur-containing amino acids -Oxidation of mercaptans	-Dimethyl sulfide -Dimethyl disulfide	Decaying cabbage Rotten cabbage	0,48 0,95	7,5 8,4	All solid wastes and ROP, except by lignocellulosic material
Volatile fatty acid	-Anaerobic biodegradation of proteins, fats, and sugars -Easy conversion into esters by hydrolysis	-Acetic acid -Butyric acid -Valeric acid	Vinegar Rancid butter Sweat	5000 4700 2200	15 0,7 0,16	MSW, OFMSW, yard trimmings, sludges, livestock effluents, and digestates
Amines		-Methylamine -Dimethylamine -Trimethylamine -Cadavérine -Putrescine	-Rotten fish -Fish -Rotten fish -Dead animal -Putrefaction	140 31 9,6	46 59 0,08	OFMSW, sludge, livestock effluents
Aromatic compound	-Desorption of molecules contained in the initial substrate -Hydrolysis of lignin (aerobic) -Biodegradation of proteins	-Toluene -Phenol -Pyridine -Scatol	-Solvent -Medical -Putrid -Fecal	0,16 1600 90 480	1300 21 200 0,03	OFMSW, sludge, livestock effluents
Oxygenated organic compound	-Decomposition under aerobic conditions of cellulose, starch, hemicellulose, pectins	-Acetone -Methanol -Ethanol	-Sweet and fruity for ketones, aldehydes, and esters -Solvent type for alcohols	30 220 200	101000 43000 990	OFMSW, livestock effluents
Terpenes	-Naturally contained in plants, they are emitted by desorption and stripping	-Limonene -α-Pinene	-Lemon -Pine tree	0,0003 0,003	210 100	Green waste. Any composted waste mixed with lignocellulosic material.

[a]Highly volatile compounds present low Henry's constants; [b]ODT: Odor detection threshold according to Van Gemert (2011); [c]Odor character varies as a function of compound content

3.3.2.1. Chemical and biological characteristics of the material

The types of chemical substances produced by the organic matrices depend on the initial composition of the compostable materials and the onset of chemical and biological transformations taking place along the biological treatments. A determinant factor for these transformations is the redox potential inside the biologically-active layer encompassing the material particles (biofilm). The redox potential governs the type of oxidation-reduction reactions occurring within the biofilm and then the final products obtained and released. Specifically, the substrates accounting for high biodegradability (high oxygen consumption or demand) generally show low redox potential.

Methane production requires a redox potential inferior to -250 mV, typically reached by sealing the biomass into digesters in the absence of oxygen. Under fully aerobic conditions, the redox potential is superior to +820 mV, thus enabling the complete oxidation of organic matter into carbon dioxide (CO_2) and water. Contrarily, the metabolites resulting from organic matter biodegradation under anoxic conditions (reductive environment) are volatile fatty acids, alcohols, formate, hydrogen sulfide, NH_3, N_2O, H_2, and others.

Reductive conditions are typically set during waste storage due to the weak gaseous exchange between the stored material and the gas interphase. Notably, redox potentials upon storage tend to drop for substrates accounting for low porosity and high biodegradability, as well as for material piled up under deficient sweeping air flows.

Although composting is considered as an aerobic process, redox potentials in the compostable material vary as a function of the depth of biofilms particle (Fig. 9). Wang et al. (2015) estimated that after 20 days of composting, the material fraction on anoxic conditions was 75% for swine manure, 50% for poultry manure and 10% for cattle manure. In general, the inner parts of the biofilm, located far from the gaseous phase, present low redox potentials and reducing conditions which are reflected in a decrease of organic matter oxidation. Blazy et al. (2014) concluded that increasing the mixing ratio bulking agent to substrate and the bulking agent's granulometry could limit the formation of anaerobic and anoxic zones and reduce the emissions of hydrogen sulfide, 2-pentanone, and 2-methyl, 1-propanol while composting slaughterhouse sludge.

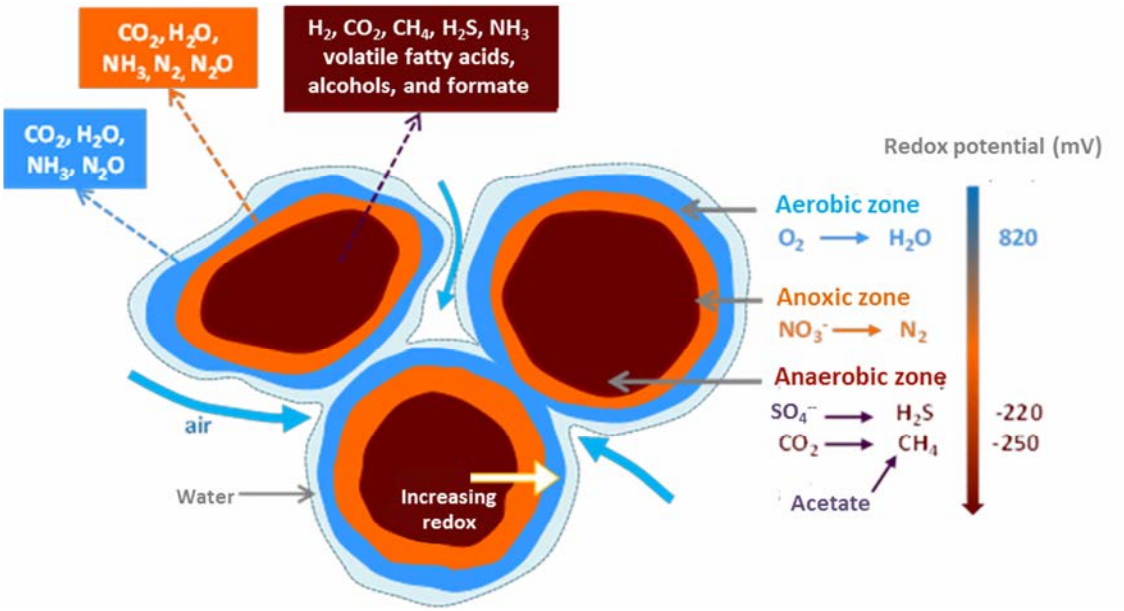


Fig. 9. Schematic representation of oxidation gradients in composting and their impacts on biological reactions and gaseous emissions (Dabert and Pourcher, 2018)

3.3.2.2. Factors influencing the gaseous exchange of odorants

Gas emissions released upon substrate storage and curing are generated in the absence of forced aeration. Hence, the volatile compounds emitted along these operational stages are principally transferred from the organic matrices toward the gas interphase by the sweeping airflows present at the storage or curing areas.

The aerobic decomposition process of organic matrices during composting requires a continuous oxygen supply (O_2). Oxygen can be supplied by i) natural aeration when the waste biodegradability is low, and the composting material account for high porosity, ii) forced aeration through insufflation or aspiration of air, and iii) regular turning of compostable material through loader or composting turner machines. In the case of forced aeration treatments, substrates are placed into enclosed or open chambers, concrete tunnels or another dispositive where a network of buried tubes is installed to inject air fresh under pressure toward the composting piles. Because of its high performance, forced aeration treatment is the most widespread composting technology at industrial scale. As a result of the microbial oxygen demand throughout the process, composting gas exhaust present lower oxygen contents than the air inflows and contains volatile compounds derived from metabolic biodegradation. The increase of aeration rates during the composting active phase triggers the transfer of metabolites from the material toward the gas interphase (Blazy et al., 2014).

The anaerobic digestion of solid waste and ROP is carried out in enclosed reactors to obtain biogas (methane and carbon dioxide). Generally, the biogas flow rates obtained upon methanization are inferior to the gas exhaust flows resulting from composting. Biogas is typically channeled for energy recovery, whereas composting emissions are conveyed to be treated through odor abatement technologies or discharge directly to the atmosphere (specifically at open-air composting).

Gaseous emissions released during pre- and post-treatment, such as extraction of the organic fraction by sorting, bulking agent addition, sieving of compostable mixtures, shredding, turning or any operation involving waste handling, have as a common characteristic that the exchange between the substrates and the gas interphase is conducted by the sweeping flow present at the ambient air. Such gaseous exchange is intensified when the material is moved, handled, or redistributed. Notably, these operations increase the functional free space air of the matrices and improve air recirculation (El Kader et al., 2007).

Beyond the type of gaseous exchange occurring between the material and the gas interphase, the transfer of volatile compounds towards the gas interphase is the greater when the compounds' Henry's constant is the lower. Table 3 provides Henry's constants for the main odor-causing compounds emitted during composting. Additionally, it should be kept in mind that Henry's constants values decline at high temperatures. Therefore, the rises in temperature, such the one observed along the active phase, can significantly augment the gaseous exchange and air pollutants volatilization.

Likewise, pH influences odor emissions. Indeed, some of the odorous compounds are acid-base pairs. When composting, pH decreases at first and then increases until 7 to 8. The initial pH is all the lower as its biodegradable content is high. Hence, depending on the pKa and pH of the medium, the odorous compounds will be preferentially in their acid or basic forms, whereas the compound responsible for odor, i.e. with the highest volatility, may be the acid or basic one.

3.4. Abatement of odor nuisances

3.4.1. Prevention of odor emissions

Diverse odorant control strategies can be designed by considering the physicochemical and biological characteristics of the material, the gaseous exchange between substrate and gas phase, and the formation of odorous compounds under certain process conditions.

Although the aerobic degradation of organic matter is not exempted from participating in the formation of odorous compounds, it is under anoxic and anaerobic conditions where most of the odor-causing compounds are produced and released. Hence, any strategy aiming at increasing the process'

redox potential leads to a decline in odorant emissions. For instance, increasing the mixing ratio bulking agent to substrate and the granulometry of bulking agents improves the composting bed porosity and air circulation which is then reflected into a decline of odorant emissions during the composting active phase (Zang et al., 2016, Yuan et al., 2015, Blazy et al., 2014, Kurola et al., 2010, Albrecht et al., 2008). Odorants are also actively generated at high moisture contents because of the free air space reduction in the material and possible compaction of the composting piles (Zhang et al., 2009; Zang et al., 2017). For aerobic treatments conducted under forced aeration, moderate aeration rates are required to prevent the formation of anaerobic/anoxic zones and simultaneously avoid excessive gas stripping of the odorous compounds. Several research works have evaluated the impact of aeration rates on odorants emissions during the active composting phase (Zang et al., 2016, Zhang et al., 2009, Sundberg et al., 2013, 2009, Li et al., 2008, Elwell et al., 2001, Fraser and Lau, 2000).

Thermal convection also influences the emission of odorants toward the atmosphere. During forced aeration treatments, the application of negative aeration (backward flow) is often employed to capture odorants emissions and avoid strict confinement of material in composting bunkers and tunnels. Nevertheless, this odorant control strategy is only partially effective because the release of odorous compounds can still occur on the composting pile surface as result of their volatilization through the upward thermal convection flow (Humeau & Le Cloirec, 2010).

The sorting and removal of some organic fractions which may be precursors of offensive odorants constitute a preventive strategy to control odor emissions along composting. This is notably the case of certain animal-derived residues (i.e., meat, fish) possibly found in MSW.

Other strategies have also been tested to prevent odorant emissions upon composting. Kurola et al. (2010) observed an aggravation on odor nuisances and diminution of the pH media while using peat as a bulking agent. Sundberg et al. (2013) proposed to inoculate composting material with mature composts. Yuan et al. (2015) reported a decrease in H_2S emissions during composting of OFMSW through $FeCl_3$ addition. According to Zang et al. (2017), the addition of nitrites and nitrates can drastically reduce the concentrations levels of H_2S, dimethyl sulfide and dimethyl disulfide at the gas exhaust.

3.4.2. Confinement, treatment and dispersion

Confinement, treatment and dispersion are the main ways developed to reduce odor nuisances. The extraction and capture of gas emissions are necessary steps to treat or dilute the produced air pollutants and consequently reduce the odor nuisance potential of discharge emissions. The feasibility of applying odor abatement strategies highly depends on the confinement of the odor emitting sources. Specifically, the level of confinement varies as a function of the employed composting technology and treatment stage.

Three major composting configurations can be distinguished: i) composting operations conducted in the absence of a barrier between the emission and the external environment such as the case of open platforms, ii) facilities where critical odor emitting operations are conducted in closed buildings, but eventually opened to perform certain waste handling operations, and iii) enclosed facilities where the aerobic treatment is carried out in confined tunnels or vessels enabling to channeled the resulting gas emissions (Fig. 10). For aerated static piles and windrows placed at open air, semi-permeable membranes and special covers can be employed to reduce the diffusion of odorous compounds (Fig. 10). Waste storage and compost curing can be similarly conducted in confined environments, for instance, closed buildings.

A **B**



Fig. 10. Concrete tunnel for in-vessel composting (**A**) aerated static pile covered by semi-permeable membranes (**B**, Gore®)

Pre- and post-treatment operations, as well as turning procedure generally required motorized vehicles (loaders) and can be performed in closed buildings or air open areas. Deficient air extraction and ventilation systems are responsible for the accumulation of hazardous and odorous pollutants in the indoor areas of composting facilities, risking plant workers health and welfare. A proper strategy to face this problem is to install several extractions points around the facility, instead of using one centralized ventilation system. Fugitive emissions at the buildings' entrances can be controlled by placing fan-powered devices (air curtains) over the doorways (Couvert and Wolbert, 2018).

The channeled outflows from confined vessels or extracted from closed buildings are typically conveyed toward chemical and odor abatement equipment and devices (Couvert and Wolbert, 2018). The emitted chemical compounds can be removed through absorption with or without oxidation (in the case of acidic, basic or oxidizing scrubbers), bio-degradation (biofilters, biolabors, percolator filters), adsorption or other processes such as catalytic oxidation. In the absence of any abatement technology, the captured or extracted gas out stream can be diluted by dispersion or condensed to remove a part of the volatile compounds. Spray solutions to mask and/or neutralize odors are also widespread at industrial

scale. Notably, the odor load level in the surrounding areas of waste treatment centers is also determined by the topography, meteorological conditions, and the distance between the odor source and exposed communities (receptors).

3.5. Odor nuisances perception

3.5.1. Odor perception

The composting gas exhaust contains several volatile compounds that can be treated, diluted or directly discharged into the atmosphere. Once released, these volatile compounds are dispersed as a function of meteorological and topography conditions. Odor nuisances are theoretically generated by compounds whose concentration is greater than their olfactory threshold (OAV>1) after dispersion. This set of odor-causing compounds will thereby be responsible for the whole olfactory sensation, determining the odor character and hedonic tone of the odor plumes.

The OAV and OC profiles of gas emissions produced during the pilot-scale aerobic treatment of FIA sludge are depicted in Fig. 11 (Blazy, 2014). If diluting the gas emissions released on the 8th day of the process by a factor of 1000 to simulate roughly the dispersion at the neighboring areas, odors would show a final OC of 500 OU_E m^{-3} and H_2S would be the molecule exhibiting the highest OAV (OAV_{max}). H_2S would be then the odorant exerting the most significant effect on odor detectability. Simultaneously, at this dilution rate, other two types of substances would present OAV>1, namely dimethyl disulfide and thiols (RSH). Hence, it is likely that entire set of odorants (H_2S, dimethyl disulfide, and thiols) would be governing the odor character and odor quality of nuisances perceived by the residents exposed under this hypothetical case.

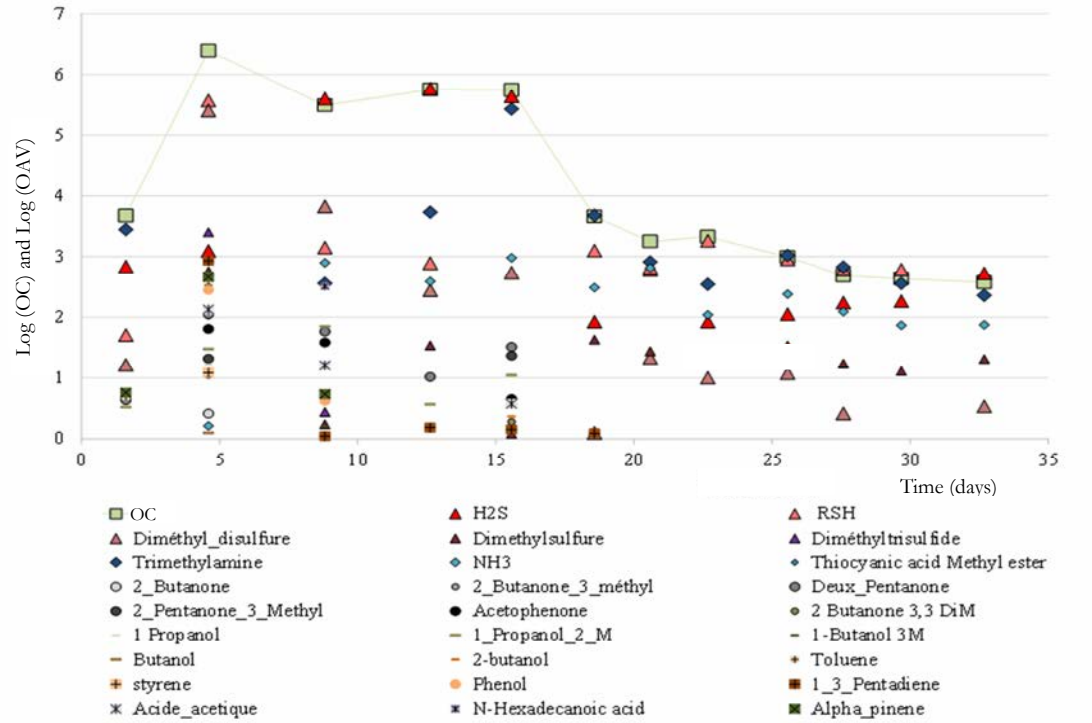


Fig. 11. OC and OAV (logarithmically transformed) as a function of time along the composting process of pig slaughterhouse sludge under forced aeration (Blazy, 2014)

3.5.2. Other factors influencing the perception of odor nuisances

Odor nuisances are triggered by the physiological response to odorants within the olfactory region of the nasal mucosa. This site contains millions of receptors cells that evoke the odor stimuli as a result of a large combination of signal responses and complex interactive effects of synergism, antagonism, among others (EN 13725, 2003; Parker et al., 2012). Human odor perception is highly subjective and it is influenced by individual and contextual factors such as the sociodemographic conditions (i.e., age, gender), specific sensibility to odors, visual perception to odor sources (image cue), and degree of awareness about the origin of odor nuisances. Pierrette and Moch (2009) found significant correlations between the discomfort felt by residents living near an animal waste treatment plant and odor properties such as odor intensity, hedonic tone, and odor frequency. Surprisingly, they also noticed that the presence of odor annoyances was highly dependent on the individual olfactory sensibility of surveyed subjects, the level of information that they had about the waste treatment process, and the image cue that residents had about the odor emitting source. Hence, to have a comprehensive picture of odor nuisances and their possible abatement, it is also necessary to take into account the personal-related factors (former exposure to odors, cognition, sensibility), the environmental stressors, and the socio-economic structure of the residential areas which may be influencing and modifying the odor sensation (Aatamila et al., 2010; Sucker et al., 2008b).

4. Characterization of odor emissions during composting process

Odors are produced throughout the entire composting process, comprising every operational step from the initial waste reception to the final compost storage (Fig.7). As previously stated in section 3.3.1., the type of emitted compounds, their concentrations and then the odorous potential of the outflow airstreams and diffused emissions are associated with the onset of organic matter transformations occurring in the initial substrate, the composting pile, and final compost. Notably, these transformations are governed by the operational conditions at the different treatment stages, and the biological and physic-chemical characteristic of the treated substrate (Cerda et al., 2018; Wei et al., 2017). The degree of dispersion and transmission of the emitted chemical compounds through the atmosphere is similarly linked with the engineering configuration of the composting plants; specifically, if the composting operations are conducted in open or enclosed facilities (Müller et al., 2004; Wei et al., 2017). For instance, in-vessel composting systems enable complete monitoring and control of the air inflow and out-going gases which are generally channeled toward an air dilution system and odor abatement facility.

However, other configurations, such as windrow composting, can be carried out in open areas, leading to immediate dispersion of the compounds emitted (Wang et al., 2009). Hence, several factors must be taken into account when evaluating and comparing odor emissions from the composting process. In the following *state-of-the-art*, the types of substrates treated, composting technology, operational stage, and air emitting source (point or diffused sources) were particularly highlighted to provide overall insight into the current knowledge on odors from this bio-engineering process.

4.1. Chemical composition and emission factors of odorants

Most of the research works on odors emissions from composting have pointed out three principal compound families as the leading causes for malodors and olfactory nuisances: volatile organic compounds (VOC), volatile sulfur compounds (VSC), and nitrogen-containing substances such as ammonia and amines (Cerda et al., 2018; He et al., 2018; Lin et al., 2018; Mao et al., 2006; Schiavon et al., 2017; Y. li Zhu et al., 2016). In turn, these odorous-causing molecules can be compiled in three categories according to their origins: i) substances initially embedded into the organic matrices that are released in the first stages of the process through the initial waste handling or stripping phenomena, ii) biogenic products resulting from microbial metabolism of organic matter, and iii) abiogenic odorants produced via chemical reactions such as pyrolysis, auto-oxidation, and Maillard reactions at high temperatures (Bidlingmaier and Müsken, 2007; Noble et al., 2001). A summary of these odorants groups is provided in Fig. 12. It is worthy to mention that xenobiotic compounds derived from anthropogenic activities can be initially present in wastes and digestates as a result of the waste production process by itself (i.e., industrial wastes), but also due to atmospherics depositions (vehicles emission) and contact of the substrates with solvent, plastics, chemical fertilizers, and fuels (Scaglia et al., 2011; Staley et al., 2006). Some of these xenobiotic

substances have low ODT (ethyl-benzene and xylene) and are then classified into odorant category one (i). Kim and Park (2008), for instance, found that ethyl-benzene was one of the most offensive odorants when assessing the emission from diverse industrial sources such as food waste treatment units.

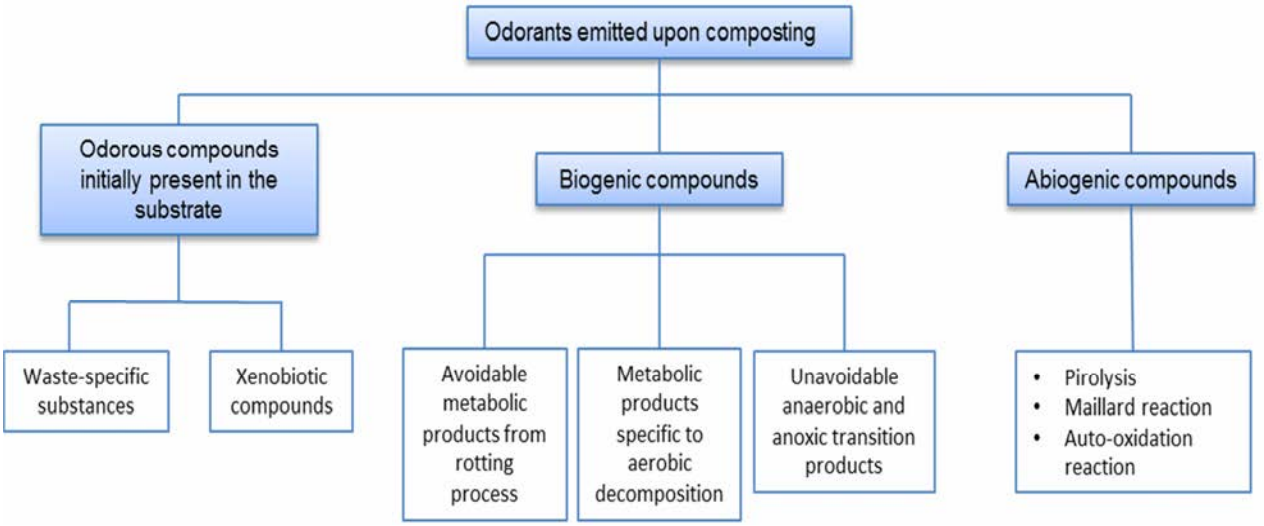


Fig. 12. Type of odor-causing compounds released during the composting process (adapted from Bidlingmaier and Müsken, 2007)

4.1.1. Volatile organic compounds (VOC)

Except for methane, VOC comprise a vast number of organic compounds exhibiting vapor pressures of at least 0.01 kPa at 20 °C and boiling temperatures inferior to 80 °C (Font et al., 2011). In composting, VOC can be originally present in the substrate or produced by metabolic reactions. Xenobiotics VOC have been detected in several types of wastes such MSW, industrial wastes, food wastes and sewage sludge (Fang et al., 2013; Komilis et al., 2004; F. Zhu et al., 2016). Aromatic compounds (BTEX), halogenated compounds (i.e., chlorinated aliphatic) and furans are the most common xenobiotics reported. Since xenobiotic compounds are recalcitrant, these type of VOC tends to be stripped and desorbed through waste handling and forced aeration process rather than decomposed along the aerobic treatment (Maulini-Duran et al., 2013b; Scaglia et al., 2011). There are also VOC naturally contained into certain organic matrices. This is the case of terpenes, such as limonene, α- and β-pinene, that are extensively linked to wastes derived from vegetable material and lignocellulosic bulking agents such as wood chip (Maulini-Duran et al., 2014; E Pagans et al., 2006).

Contrarily, biogenic VOC are produced during the anaerobic and aerobic metabolism of the organic matter. The partial aerobic degradation of organic matrices leads to the formation of ester, ketones, alcohols, organic acids, sulfide compounds, amines (Gallego et al., 2012; Schiavon et al., 2017). Some of the specific mechanisms of production for biogenic VOC are listed in Table 3. Scaglia et al. (2011) claimed that anaerobic and partial-aerobic respiration occurring in the bio-film particles of compostable material

was the principal mechanisms for VOC production upon composting of MSW. These authors also reported that VOC emissions peak during the first weeks of aerobic treatment when the oxygen consumption is the highest, thus proving a strong link among the production of these molecules and microbial activity. Such finding has also been confirmed by some authors (Krzymien et al., 1999; Maulini-Duran et al., 2014, 2013b) who describe the transition from mesophilic to thermophilic conditions, typically occurring during the early days of the active composting phase, as the ruling stage where most of the VOC are discharged. On the other hand, Stanley et al. (2006) and Eitzer et al. (1995) observed that gas spearing (stripping) could play a vital role in volatilizing VOC previously generated throughout the first stages of waste treatments where no artificial aeration is supplied (collection, reception, transport, and storage).

Concerning odors, VOC have been commonly regarded as significant sources of odor pollution during composting operations because of their high volatility, large capacity to diffuse through the atmosphere, and, in some cases, low ODT. Scaglia et al. (2011) demonstrated that there was a close correlation between OC measurements and VOC emissions (r= 0.96) and underlined the relevance of these substances as odor contributors for MSW composting. Likewise, VOC such as p-cymene, dimethyl sulfide, acetic acid, ethylbenzene, and trimethylamine have been highlighted as critical odor components in the boundaries and indoor areas of food waste composting plants (Mao et al., 2006; Tsai et al., 2008). A relevant study evaluating the odor impact of VOC emissions along the composting process at laboratory scale was recently performed by Schiavon et al. (2017). According to this research work, the molecules accounting for the largest OAV and odorant potential upon the aerobic treatment of sewage sludge, MSW, and food waste were dimethyl sulfide, limonene, and ethyl isovalerate, respectively. Unlike these results presented by Schiavon et al. (2017), Fang et al. (2013) revealed that volatile fatty acids (VFA) were the major odorants among 72 VOC identified in a mechanical-biological treatment plant (MBT) processing MSW. Evidently, the process conditions, the intrinsical differences in the waste composition, and the variability in the employed analytical methods may have caused the variation on these reported chemical-odor fingerprints. Terpenes, particularly limonene, have also been identified as critical odor-causing compounds during the curing process of composted MSW (Dorado et al., 2014), the storage of green waste (Agapiou et al., 2016), and the composting process of biowaste (Müller et al., 2004).

One main criticism for most of the studies focusing on VOC emissions and their link with odor generation is that they generally draw conclusions about olfactory nuisances without taking into account other critical volatile inorganic odorants such as ammonia and H_2S. This fact was corroborated by Colón et al. (2017). In this study, the authors related OC measurements with both, VOC and H_2S, for indoor air emissions at different areas of a MBT plant treating MSW (reception warehouse, pretreatment, anaerobic digestion, and composting areas). Although some VOC such as 2-pentanone, eucalyptol, dimethyl sulfide,

and decanal exceeded their ODT, H_2S was reported as the leading odorant in all evaluated areas, except for the pretreatment compartment.

4.1.2. Volatile sulfur compounds (VSC)

VSC are a group of sulfur-containing molecules that gathers both, volatile inorganic sulfur compounds (VISC) such as H_2S and carbon disulfide (CS_2), and volatile organic sulfur compounds (VOSC). These substances have drawn the attention of odor assessment studies in composting operations because of their extremely low ODT (Table 3) and high occurrence frequencies (Han et al., 2018; He et al., 2018; Zang et al., 2016; Y. li Zhu et al., 2016). The VSC most commonly detected in composting facilities are H_2S, dimethyl sulfide (DMS), dimethyl disulfide (DMDS), methanethiol (MeSH), ethanethiol, CS_2, dimethyl trisulfide (DMTS). In general, VSC are generated under anaerobic conditions prompted in the biofilm-particles of the composting piles. Reducing conditions are associated with the depletion of oxygen along the organic matter decomposition process (Scaglia et al., 2011), but also with operational conditions favoring the formation of anaerobic microsites such as insufficient aeration, poor substrate mixing, and the presence of very wet zones (Smet et al., 1999).

The production mechanisms for some relevant VSC are depicted in Fig. 13. The principal step for VSC production is the anaerobic degradation of sulfur-containing amino acids present in the treated substrates. Cysteine and methionine are anaerobically degraded into H_2S and CH_3SH, respectively. Methanethiol can be then transformed into DMS through anaerobic methylation. In contrast, DMDS is expected to be formed through the abiotic oxidation of DMS whenever aerobic or partial-aerobic conditions are set. VSC are also precursors from each other due to the coupled methylation and demethylation of these compounds under reducing conditions. VOSCs are broken down by anaerobic bacteria, such as the methanogen degraders, to generate H_2S. Besides protein and VOSCs degradation, sulfate reduction is another remarkable mechanism for H_2S generation, principally conducted by the sulfur-reducing microorganism. H_2S is therefore seen as one of the principal end-products from the sulfur cycle at the furthest stages of waste processing (Drennan and DiStefano, 2010; Higgins et al., 2006; John T Novak et al., 2006). It is worthy to mention that temperature and pH of the composted media are important parameters regulating the acid-base equilibrium and volatility of VSC in the biofilm-particles (ADEME, 2012). Regarding DMS production, there is currently a scientific debate about the abiotic or biotic origin of this molecule. He et al. (2018) observed that DMS and DMDS emissions steadily increased at the end of the aerobic treatment of sewage sludge when the oxygen level and bio-stability degree were the highest, thus suggesting that the formation of both VSC could be principally triggered under aerobic-abiotic conditions.

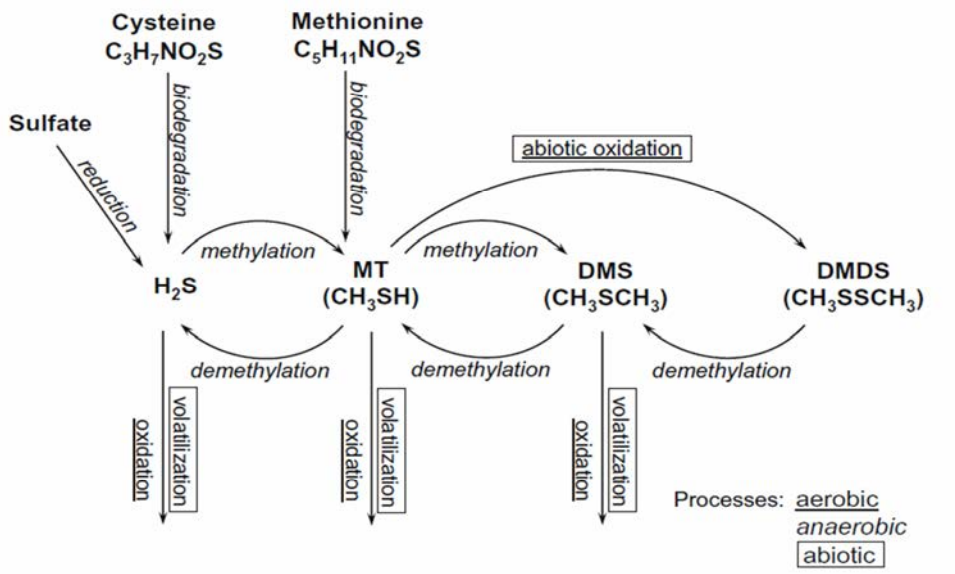


Fig. 13. Production and degradation of principal volatile sulfur compounds (Drennan and DiStefano, 2010)

The establishment of anaerobic microsites at the composting piles is almost unavoidable even if suitable aerations rates and other good composting practices are implemented (Wei et al., 2017). Zhang et al. (2016) proved that VSC emissions could be drastically controlled to low emission levels through the application of suitable aeration rates. However, VSC account for extremely low ODT that make them significant sources for odor annoyances in waste treatment operations even at very low concentrations. This fact has been demonstrated by several authors. Zhu et al. (2016) selected DMDS (concentration range: 0-12 mg m^{-3}) as a core indicator for odor pollution in an aerated static pile stabilizing sewage sludge. Although higher H_2S emissions were detected in this study (range: 2-40 mg m^{-3}), only DMDS was detected at the surrounding areas of the composting facility (1 km). DMS and DMDS have been similarly identified as critical odor components throughout sewage sludge composting (Durme et al., 1992; Schiavon et al., 2017) and digestate sludge composting (Maulini-Duran et al., 2013a) at laboratory and plant-scale. Conversely, Han et al. (2018) showed that H_2S and CH_3SH were the principal cause for odor nuisances when assessing gas emissions from a municipal composting plant treating sewage sludge at different seasons (winter, spring, and summer). The overall odor contributions for these odorants, calculated through OAV, fluctuated from 20% to 54%.

For other organic matrices such as food waste and MSW, some discrepancies have also been reported when characterizing the main VSC responsible for odor episodes along with their aerobic treatments. Some research works have identified DMDS and DMS as the main odor-causing compounds for food waste composting plants (Mao et al., 2006; Tsai et al., 2008), whereas Zhang et al. (2013) concluded that H_2S was the most abundant VSC emitted during the biological stabilization of kitchen waste and MSW by representing from 39 to 43 % of the cumulated mass emissions. As a result of its substantial contribution to odor generation, H_2S was also included in a multivariate regression model developed to predict OC in

an MBT facility composting MSW (Colón et al., 2017). It appears that H_2S is extensively produced at the MSW composting cells (1.7-3.2 ppmv) and other storage compartments involved in the final compost refining (<0.1 ppm) (Moreno et al., 2014). Sun et al. (2017) affirmed that H_2S was responsible for 95 % of odor annoyances at different sampling points from an MSW transfer and reception stations.

Once more, the considerable variation in results from studies dealing with similar organic substrates is linked with the differences in the composting technologies and process scales, operational conditions, waste composition and type of analytical methods used to trace odors. Notably, some of the mentioned studies are focused on VOSCs analysis (i.e., GC/MS), and the possible influence of H_2S on odors was sometimes neglected.

4.1.3. Ammonia

During the aerobic treatment of solid wastes, molecules containing organic nitrogen (N_{org}), such as proteins, amino acids, and urea, are mineralized by microorganism settled down in the compostable media. This process, also called ammonification (1), results in the release of free ammonium (NH_4^+/NH_3) (Fig. 14). In turn, this nitrogen in the form of NH_4^+/NH_3 can be immobilized (2) by the biomass to synthesize organic compounds indispensable for microbial growth (i.e., proteins). The ammonification rate in composting is generally higher than the immobilization turnover, thus causing an accumulation of NH_4^+/NH_3 (Zeng et al., 2012b). The NH_4^+/NH_3 initially contained in the compostable substrates and the one accumulated upon the ammonification process can be consequently stripped and volatilized (3) as NH_3, nitrified-denitrified (4 and 5), or simply stored and transferred toward the organic matrices and leachates. Ammonia volatilization and stripping constitute one of the principal causes for nitrogen losses during composting of organic matrices, especially for those raw substrates accounting for low carbon to nitrogen (C/N) ratios. De Guardia et al. (2010) evaluated the nitrogen dynamics during composting of five wastes, revealing that nitrogen losses as NH_3 could represent up to 83% of the total nitrogen removed from compostable materials. These authors also showed that the nitrogen losses increased through the application of higher aeration rates. Likewise, Jiang et al. (2011) observed that 9.4-32 % of the total nitrogen was mainly lost in the form of NH_3 during pig manure composting. Nitrogen losses are not only traduced into a decline of the compost quality (less nutritive and agronomical value) but also the release of odorous and hazardous gaseous emissions containing NH_3 and nitrous oxide (N_2O). Although N_2O is rather odorless, this substance is a potent greenhouse gas exhibiting a warming potential 293 times superior to that of CO_2 (Hao and Benke, 2008). N_2O is produced as an intermediary of both, nitrification and denitrification process (4 and 5). Regarding ammonia, its volatilization and stripping are regulated by the composting conditions. Pagans et al. (2006) noted that high temperatures and pH prompted the ammonia volatilization in the biofilm by moving the NH_4^+/NH_3 equilibrium toward the NH_3 form. The deposition of NH_3 in the atmosphere and ecosystems can lead to the eutrophication of surface waters,

reduction of the air quality, formation of smog and acid rain, and generation of odors nuisances (Hao and Benke, 2008; Zeng et al., 2012a).

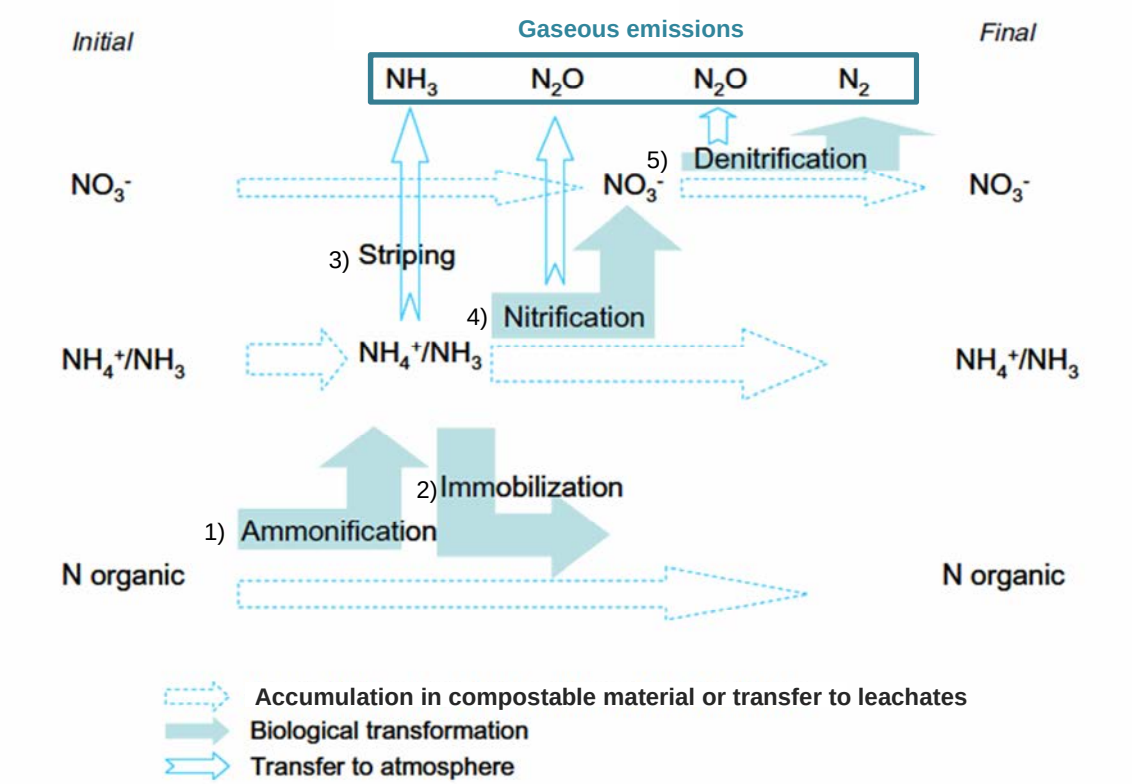


Fig. 14. Nitrogen transformations and major nitrogen species released during composting (adapted from de Guardia et al., 2010)

Ammonia is actively released along the aerobic treatment of organic matrices accounting for low C/N ratios such as food waste, sewage sludge, MSW and anaerobically digested substrates (Cerda et al., 2018; Krzymien et al., 1999; Zang et al., 2016; Zeng et al., 2016). Despite its high ODT (1.4 mg m^{-3}), NH_3 is generally present in the gas exhausts from composting operations at concentrations above this odor detection limit (Lin et al., 2018; Pagans et al., 2006; Wei et al., 2017). For instance, Moreno et al. (2014) and Zhu et al. (2016) detected gaseous emission with NH_3 levels of 418 and 150 mg m^{-3} within the first two weeks of the composting process of MSW and sewage sludge, respectively. Hort et al. (2009) observed that the windrow composting of a mixture consisting of sewage sludge and yard trimmings (1:3, wet mass basis) gave rise to the formation of NH_3 at levels (50 mg m^{-3}) largely exceeding its ODT and health threshold limit value (3.9 mg m^{-3}). Even if ammonia is not normally considered as the major odorant compound during waste processing, several authors have highlighted its contribution to olfactory nuisance when composting pig slaughterhouse sludge (Blazy et al., 2014), food waste (Tsai et al., 2008), sewage sludge (He et al., 2018) and pig manure (Hanajima et al., 2010). On the other hand, Schlegelmilch et al. (2005) estimated that the NH_3 concentration in the gas exhaust of a biowaste composting facility had

a minor influence on the overall odor concentration. According to this research work, NH_3 exhibited an OAV that was 100 times inferior to the measured OC (10^5 OU_E m^{-3}).

4.1.4. Emission factors and chemical concentrations of odorous compounds

A comprehensive summary of research works evaluating the main odorants detected upon composting is presented in Table 4. This bibliographic compilation was focused on the main odor-causing compounds released during composting: VOC, VSC, and NH_3. The maximum concentrations, emission factors (i.e., cumulative mass emission) and odor activities values of the major odorants were presented if reported in the consulted literature. Some of the most important operational and sampling conditions were similarly highlighted to provide overall insight into the global trends on odorants assessment. The included operational and sampling conditions were the composting stage (i.e., aerobic treatment, turning, sieving, etc.), the study scale (laboratory or industrial scale), the use of bulking agent (B.A) to conduct the biological treatment, and the type of emission sources sampled; that is, whether the study evaluated channeled airstreams (point sources) or diffused air emissions (area sources). Since odor pollution is highly dependent on the substrate composted, the type of organic matrices treated was also underlined. To this end, a total of 32 relevant publications were herein consulted.

Table 4. Chemical concentration (max. conc.), emission factors, and odor activity values of main odorants reported upon composting of solid waste and digestates

Type of waste	Operational/sampling conditions[a]				Target compound[b]			Major odorant[c]	Max. Conc. (mg m^{-3})	Emission factors[d] (mg kg^{-1}WB)	Max. Odor activity value (OAV)[e]	Reference
	B.A	Stage	Source	Scale	VOC	VSC	NH_3					
Sewage sludge	x	Aeration	Point	Ind	x	x	x	DMS	2.7	-	1026	Durme et al. (1992)
	x	Aeration	Point	Lab	x			DMDS	22.5	-	6818	Schiavon et al. (2017)
	x	Aeration	Point	Ind.		x	x	MeSH	3.8	-	18095	Hort et al. (2009)
	x	Aeration	Point	Lab		x		MeSH	-	0.08	2987	He et al. (2018)
	x	Aeration	Area	Ind	x	x	x	DMDS	12	-	5454	Zhu et al. (2016)
	x	Aeration	Point	Ind		x		H_2S	-	10.3-18.9	50% (PO_i)	Han et al. (2018)
	-	Storage	Point	Lab		x		MeSH	800	-	-	Xu et al. (2011)
Anaerobically digested (AD) sewage sludge	-	Storage	Area	Ind		x		MeSH	8	-	38095	Fisher et al. (2018)
	x	Aeration	Point	Lab	x		x	DMDS	0.05	0.001	5.9	Maulini-Duran et al. (2013a)
	-	Storage	Point	Lab		x		MeSH	163	-	776190	Novak et al. (2006)
Food waste	x	Aeration	Point	Lab	x			Ethyl isovaleriate	31.5	-	422818	Schiavon et al. (2017)
	-	Aeration	Point	Lab		x		H_2S	-	35.6	-	Zhang et al. (2013)
	x	Aeration	Both	Ind	x	x	x	Trimethylamine	13	-	21000	Tsai et al. (2008)
	x	Aeration	Both	Ind	x	x	x	Amines	72	-	12040	Mao et al. (2006)
	x	Aeration	Point	Lab		x		H_2S	-	98	-	Zhang et al. (2016)
	-	Storage	Area	Ind	x	x		Acetaldehyde	0.01-0.5	-	10	Ni et al. (2015)
	x	Aeration	Point					MeSH	0.21	-	1500	
Municipal solid waste (MSW) and organic fraction of MSW (OFMSW)	x	Sieving	Area	Ind	x	x	x	Isovaleric acid	-	-	27% (PO_i)	Fang et al. (2013)
		Aeration	Point					Isovaleric acid	-	-	33% (PO_i)	
	x	Aeration	Point	Ind	x	x	x	H_2S	5.5	-	13414	Moreno et al. (2014)
		Curing	Point					H_2S	0.15	-	366	
	x	Aeration	Point	Lab		x		H_2S	-	30.5	-	Zhang et al. (2013)
	-	Storage	Point	Ind	x	x		H_2S	0.75	-	1250	Colón et al. (2017)
	-	Sieving	Point					DMDS	0.07	-	8.2	
	x	Aeration	Point					H_2S	1.35	-	3375	
	x	Aeration	Point	Lab	x			Trimethylamine	0.27	-	269	Scaglia et al. (2011)
	-	Storage	Area	Ind	x	x	x	H_2S	0.06	-	127	Sun et al. (2017)
	-	Curing	Point	Ind	x			Limonene	11.4		50	Dorado et al. (2014)
	x	Aeration	Both	Ind	x			3-methyl-butanol	10^{-5}	-	-	Fischer et al. (2008)
	x	Turning										
Biowaste and Green waste	-	Aeration	Area	Ind	x			Limonene	0.02	-	0.11	Müller et al. (2004)
	-	Aeration	Point	Ind	x	x	x	DMS	8.2	8.2	1367	Smet et al. (1999)
	-	Aeration	Area	Ind	x		x	Fatty acids	16.3	-	14000	Rosenfeld and Suffet (2004)
	-	Storage	Area	Ind	x			Limonene	-	-	-	Agapiou et al. (2016)
Pig S. sludge[f]	x	Aeration	Point	Lab	x	x	x	H_2S	-	899	10^5-10^6	Blazy et al. (2014)
Pig manure	x	Aeration	Point	Lab	x	x	x	MeSH	61.8	-	417267	Hanajima et al. (2010)
AD biowaste	-	curing	Point	Lab		x		H_2S	183	-	-	Drennan and DiStefano (2010)
AD OFMSW	-	storage	Area	Ind	x		x	p-cymene	3.8	-	32	Orzi et al. (2010)

[a]B.A: crossed if bulking agent was added, Forced aeration treatment (Aeration); [b]Volatile organic compounds (VOC), volatile sulfur compounds (VSC), and ammonia. [d]Emission factor expressed as a ratio of the initial mass of substrate composted on a fresh mass basis (WB). [e]PO_i: Percentage of odor contribution calculated with OAV, $PO_i = OAV_i/\sum OAV_t$. [f]Pig slaughterhouse sludge.

As shown in Fig. 15, 63% of the consulted research work addresses the identification and quantification of odorants along the aerobic treatment of organic matrices, thus representing the most studied operational stage. Forced aeration treatments are typically regarded as one of the main steps for odor generation at both, laboratory and industrial scale (Table 4). Several authors have shown that the first days of the aerobic treatment are responsible for the rise of odor nuisances as a result of odorants generation (biotic and abiotic), the increase of the pile temperature and the stripping of initial embedded odorous compounds (Gutiérrez et al., 2015a; Scaglia et al., 2011)

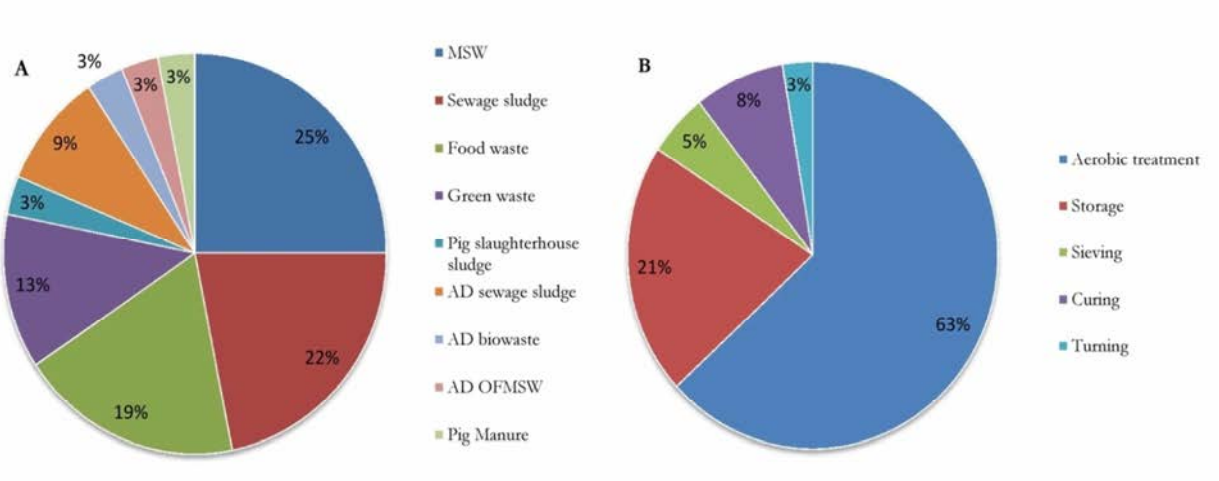


Fig. 15. Organic matrices (**A**) and operational stages (**B**) commonly assessed on studies dealing with odorants emissions from composting process

In contrast, the odor and environmental impact of gas emissions from other critical steps involved in the biological treatment of organic matrices has been scarcely estimated (Fig. 15). For instance, only 23 % of the consulted investigations analyzed odorants emissions from waste and digestate storage. The occurrence of VSC and strong odor nuisances have been reported while storing MSW (Colón et al., 2017) and biosolids (Fisher et al., 2018; Novak et al., 2006). Moreover, the odorant emission potential throughout the turning process was only investigated by Fischer et al. (2008) who provided the OC profiles and concentrations of eight biogenic VOC. The analytical methods employed in this investigation did not allow bringing conclusions about the molecules involved in the odor episodes. Hanajima et al. (2010) identified the dominant odor contributing components during forced aeration treatment of a mixture of pig manure and paper (65%), and the influence of turning on odor evolution. These authors demonstrated that the turning of compostable material leads to an increase on OC and methanethiol concentrations for the following days of the aerobic treatment. Such a lack of emission inventories when performing the turning process is principally related to the methodological complexity of gas sampling during this particular operational procedure.

The chemical composition of odor emissions has been principally assessed when composting MSW, sewage sludge, food waste and green wastes (Table 4). Still, an upward trend is evidenced concerning the number of investigations dealing with the odor-causing compounds from composting of anaerobically digested (AD) substrates (Table 4). The number of published articles on this subject has risen from one in 2006 to four after 2010. Composting of AD sewage sludge was undoubtedly the most studied process, accounting for 9% of the consulted research works. The current boomed of the anaerobic digestion market, and the need of managing properly the produced digestates is reflected in an increasing interest in composting as a suitable post-treatment technology (Arab and McCartney, 2017; Zeng et al., 2016). As reported in the articles consulted (Table 4), the final stabilization process of digestates through aerobic treatments, curing and storage are associated with odor pollution. However, compared to raw substrates, digestate composting and the olfactory impact of the generated odorous gas emissions along this post-treatment have been poorly studied.

In general, around 70% of the consulted research works included whether VOC or VSC analysis in their odor monitoring strategies, whereas only 22% of the publications offered a complete odorant composition profile comprising VOC, VSC, and NH_3. Such analytical limitation can give rise to misleading conclusions when assessing the principal components of malodors at waste treatment units. VSC, and particularly H_2S (34%), have been widely reported as the main odorous compounds from the composting process with disparate maximum concentrations ranging from 0.05 up to 800 mg m^{-3}. A large variability of identified odorants and concentrations is documented even through the treatment of the same type of organic matrices and operational stage. In the case of the forced aerobic treatment of MSW (Table 4), H_2S, isovaleric acid, and trimethylamine were selected as the key odorous compounds (Colón et al., 2017; Fang et al., 2013; Moreno et al., 2014; Scaglia et al., 2011). Such discrepancies on odorants inventories are caused by the differences on waste composition and operational conditions (i.e., air inflows, mixing rate with bulking agent), the type of analytical methods used, and the gas sampling methodology (point or area sources). It is worthy to mention that 60% of the investigations consulted were carried out at an industrial scale where other external factors such as the weather conditions, the presence of leakages (fugitive emissions) and airstreams dilutions, can drastically influence results from odorants measurements. To face this large variability on data, Schiavon et al. (2017) performed bench-scale composting experiments to characterize and compare VOC and their odorant potential while aerobically treating sewage sludge, MSW, and food waste under the same operating conditions. In this study, important odorants such as NH_3 and H_2S were not considered, and the assumption that all compostable materials required the same aerobic treatment was taken. Few efforts have been devoted to analyze and compare odorant emissions from different compostable substrates at controlled pilot and bench conditions despite their importance to unify data and establish reliable odorants inventories.

Emission factors, relating the cumulative mass of compound emitted to the initial amount of organic substrate treated, have not been frequently reported in the literature addressing odor pollution at waste

treatment units (Table 4). Compounds fluxes and rates are fundamental input data to design composting facilities and odor abatement units, develop dispersion models of pollutants, and establish comparisons among biological treatments at different scales (Cadena et al., 2009; Maulini-Duran et al., 2013a). A limited number of VOC and NH_3 emissions factors have been provided for the forced aerobic treatment of biowastes, sewage sludge and MSW (Cadena et al., 2009; Maulini-Duran et al., 2013a; E Pagans et al., 2006; Shao et al., 2014; Staley et al., 2006) ; yet, they are not directly linked to odor generation. On the other hand, there is currently a growing number of publications that highlight the vital role of VSC on odor management at composting facilities and provide emission factors for these odorous molecules (Han et al., 2018; He et al., 2018; Zhang et al., 2016, 2013).

In conclusion, further research is required to fill the gap of knowledge on the chemical composition of odorous gas emission along the different operational stages of composting of solid wastes and digestates. A significant variability of results was observed regarding the type of odor-causing compounds and their concentrations in the consulted scientific literature. However, few studies have tackled this problematic by evaluating odorants emissions while composting different organic matrices at controlled pilot and bench conditions. Also, there is a strong need for broadening the emission factors inventories upon composting of various organic matrices, focusing not only on VSC or VOC, but considering the entire spectrum of odorous compounds (VOC, VSC, and NH_3). Finally, as a result of the flourishing of anaerobic digestion industry, more extensive efforts must be made for describing the odor and environmental impact of gas emissions released along the different operational steps of digestates post-treatment through composting.

4.2. Odor concentration (OC), odor emission rates (OER), and odor emission factors (OEF)

Nowadays, odor monitoring is progressively playing a pivotal role in waste management and composting research. This tendency is proved by the increasing number of studies that perform sensory measurements at the laboratory and industrial scale, going from ten publications before 2010 to 14 reports in the last eight years. Particularly, the forced aeration treatment of solid wastes is the process stage most widely monitored, being addressed by 96% of the research works summarized in Table 5. In contrast, OC inventories for gas emissions released along other process steps such as storage, sieving, turning, and shredding are limited, being reported in only 4 to 20 % of the examined literature. There is also a clear preference for assessing the gas emission produced during the biological process of MSW (31%), sewage sludge (21%), and green waste (17%). However, odor emissions produced when composting agro-industrial wastes such as animal manures and horticultural wastes have been recently investigated (Blazy et al., 2015; Gutiérrez et al., 2017a; Hanajima et al., 2010; Toledo et al., 2018).

Table 5. Odor concentration (OC) and odor mission rates (OER) reported in the scientific literature concerning gas emissions from solid waste and digestate composting

Type of waste	Operational/sampling conditions[a]				Major odorants[b]	OC[c] (OU_E m^{-3})	OER[c] (OU_E s^{-1})	Reference
	B.A	Stage	Source	Scale				
Sewage sludge (SS)	x	Aeration	Area	Ind	DMS	152-161	-	Durme et al. (1992)
	-	Sieving	Area			25	-	
	x	Aeration	Point	Lab	-	3549	0.15	Gutiérrez et al. (2017b)
	x	Aeration	Area	Ind	DMDS	100-650	-	Zhu et al. (2016)
	x	Aeration	Point	Lab	-	-	0.1-0.5	Toledo et al. (2018)
	x	Aeration	Point	Ind		6500-151800	-	ADEME (2012)
Anaerobically digested (AD) sewage sludge	-	Storage	Point	Lab	MeSH, DMS	1000-8500	-	Higgins et al. (2006)
Food waste	-	Shredding	Area	Ind	TMA, VSC	2523-3577	-	Di et al., (2013)
	x	Aeration	Area	Ind	NH_3, TMA, DMS, acetic acid	306-546	-	Mao et al. (2006)
	-	Shredding	Area	Ind	H_2S, TMA	253-6000	-	Wu et al. (2015)
Municipal solid waste (MSW) and organic fraction of MSW (OFMSW)	x	Aeration	Point	Ind	VSC, fatty acids	9000-46000	10^5-10^6	Gutiérrez et al. (2015a)
	x	Aeration	Area	Ind	-	30-5224	11000	Gutiérrez et al., (2015b)
	x	Aeration	Point	Lab	-	31144	1.7	Gutiérrez et al. (2017b)
	-	Reception	Area	Ind	-	2786	320000	Sironi et al. (2006)
	x	Aeration	Point			10079	(total)	
	-	Curing	Area			1071		
	-	storage	Area			414		
	-	Sieving	Area	Ind	-	1253-16400	-	Fischer et al. (2008)
	x	Aeration	Point			1000-10000		
	x	Turning	Area			1117-4000		
	x	Aeration	both	Ind	-	57-24000	-	Biasioli et al. (2004)
	x	Aeration	Point	Lab	-	-	0.5-3.9	Toledo et al. (2018)
	-	Storage	Point	Ind	H_2S	2277-6379	-	Colón et al. (2017)
	-	Sieving	Point			387-12358		
	x	Aeration	Point			2276-6531		
	x	Aeration	Point	Ind	VSC	2067-32944	-	Scaglia et al. (2011)
AD OFMSW	-	Storage	Area	Ind	p-cymene	-	1.4	Orzi et al. (2010)
Biowaste and Green waste	x	Aeration	Area	Ind	-	1000-190000	-	Schlegelmilch et al. (2005)
	-	Aeration	Area	Ind	Ester, ketones	390-13050	-	Defoer et al. (2002)
	-	Shredding	Area	Ind	–	130-500		ADEME (2012)
	x	Aeration				440-3265		
	-	Curing				170-1240		
	x	Aeration	Point	Lab	VSC	4900-12400	-	Krzymien et al. (1999)
Pig slaughterhouse sludge	-	Storage	Point	Lab	TMA,H_2S, MeSH	4000-80000	-	Blazy et al. (2015)
	x	Aeration				300-4000000		
	x	Curing				544-2400		
Agro-industrial waste plus SS	x	Aeration	Point	Lab	-	1000-30000	0.1-3.5	Gutiérrez et al. (2017a)
	x	Aeration	Point	Lab	-	-	0.1-1.4	Toledo et al. (2018)
Horticurtural wastes	x	Aeration	Point	Lab	-	853-28525	0.1-1.1	Gutiérrez et al. (2017b)
Poultry and horse manure	x	Aeration	Area	Ind	H_2S, DMS	666-20139	-	Noble et al. (2001)
Pig manure	x	Aeration	Point	Lab	MeSH	1000-316000	-	Hanajima et al. (2010)

[a]B.A: crossed if bulking agent was added, Aeration: Forced aeration treatment; [b] VSC: Volatile sulfur compounds, MeSH: Methanethiol, DMS: Dimethyl sulfide, DMDS: Dimethyl disulfide, TMA: trimethylamine; [c] Range (minimum to maximum value) or mean (single value) OC and OER.

The OC evolution along the forced aeration treatment of solid wastes has been widely documented by several authors. The oldest reports describing OC dynamics during the aerobic treatment are the ones provided by Durme et al. (1992) and Krzymien et al. (1999) who noted that the first two weeks of the composting process were responsible for odor emissions peaks and VOC releases, presumably due to an increase in the microbial activity on that treatment stage (hydrolytic phase). These authors also observed that odors tended to decline as the biological process proceeded. In line with these studies, Schlegelmilch et al. (2005) observed that the principal event of odor pollution occurred within the first week of biowaste composting (OC_{max}= $1.9 \cdot 10^6$ OU_E m^{-3}) which was followed by an OC drop (<10^3 OU_E m^{-3}) at the end of the biological treatment. These authors did not find a link between OC profiles and some microbial activity indicators such as carbon dioxide and oxygen concentrations, and temperature. Some years after, Scaglia et al. (2011) demonstrated that odors and VOC emission were closely correlated to the oxygen consumption (represented as the dynamic respiration index-DRI) and thus to the biological stability of MSW while being composted (r> 0.96, n=6). This finding was then confirmed by Gutiérrez et al. (2014) who revealed a parallel evolution of the temperature, OC and microbial activity (expressed as DRI) when aerobically treating the organic fraction of MSW (OFMSW) in a dynamic respirometer (OC vs. DRI, r=0.9, n=22). Recently, close relationships among OC and OER profiles and biological stabilization indicators have also been obtained along the aerobic treatment of sewage sludge, horticultural wastes, and agro-industrial wastes (Gutiérrez et al., 2017b, 2017a; Toledo et al., 2018).

The amount and type of odor-causing compounds emitted during composting are directly reflected in the levels of OC and OER. Hence, the operational and sampling conditions, as well as the composition and nature of the substrates treated are key factors not only influencing the production and release of certain chemical species, but also regulating the olfactory perception. Despite the remarkable importance of describing OC and OER evolution together with the chemical fingerprints of gas emissions, only 60% of the literature consulted provides complete sensory and odorant assessments. VSC, trimethylamine, and fatty acids are commonly identified as significant drivers of the odor nuisances at composting plants (Table 5).

The reported OC and OER values vary greatly even for the same type of treated organic matrices and composting stage evaluated (Table 5). For example, throughout the aerobic treatment of sewage sludge, point source emissions presented maximum OC that ranged from 3549 to $1.5 \cdot 10^6$ OU_E m^{-3}, whilst diffused emissions (area source) accounted for OC fluctuating from 161 to 650 OU_E m^{-3}. Likewise, a large variation on reported OC_{max} has been evidenced during the composting active phase of green waste (3645-$1.9 \cdot 10^6$ OU_E m^{-3}) and MSW (6531-$4.6 \cdot 10^5$ OU_E m^{-3}). In particular, the composting process of pig slaughterhouse (Blazy et al., 2015) and pig manure (Hanajima et al., 2010) recorded maximum OC of $3.1 \cdot 10^5$ OU_E m^{-3} and $3.1 \cdot 10^6$ OU_E m^{-3} (point sources), respectively, thus leaving in evidence the tremendous potential of these substrates on the rise of odor annoyances through their aerobic

stabilization process. Comparing odor data among diverse studies is extremely complex because of the inherent variability in odor measurements when applying different composting and operational conditions. To establish comparisons among different substrates biodegradability and odors, Gutiérrez et al. (2017b) and Toledo et al. (2018) performed dynamic respirometric tests on OFMSW, horticultural wastes and sewage sludge. These authors concluded that organic matrices accounting for the highest biodegradability (expressed as cumulative oxygen consumption), such as OFMSW, exhibited the maximum odor generation rates. Similarly, Blazy et al. (2014) stated that aeration rates have an instant effect on volatile compounds and OC levels by increasing odorants stripping and waste biodegradability.

The aeration rate is a significant parameter governing the aerobic treatment, the stripping phenomena, and level of dilution of the gas outflow. This parameter can be integrated into odor assessments through the calculation of the odor emission rates (OER in $OU_E\ s^{-1}$). OER is defined as the product of OC and the exhaust gas flow rate of a source (point or area). This term describes more accurately the odor evolution along the composting process as a function of the resulting outflows and provides input data for dispersion models (Laor et al., 2014). Nevertheless, only seven reports out of 24 consulted articles calculated and provided OER (Table 5). The reported OER from composting of MSW, sewage sludge, and horticultural wastes at a bench scale, are much less variable than OC, ranging from 0.1 up to 3.9 $OU_E\ s^{-1}$ (Gutiérrez et al., 2017b, 2017a, 2014; Toledo et al., 2018). Evidently, OER are also dependent on the amount of waste being processed. This fact may explain the observed differences between the maximum OER found during the aerobic treatment of MSW at the laboratory (1.7-3.9 $OU_E\ s^{-1}$) and industrial scale (10^3-10^6 $OU_E\ s^{-1}$). Odor emission factors (OEF in $OU_E\ kg^{-1}$) can thus ease the inter-comparison among studies carried at different scales by linking the overall amount of odor produced with the initial amount of substrate treated. In that sense, OEF is a similar term to the emission factors discussed in section 4.1.4. OEF have been principally assessed during the odor monitoring of a WWTP (Capelli et al., 2009), pig house (Schauberger et al., 2013), and landfill (Lucernoni et al., 2016). Sironi et al. (2006) conducted the only current investigation evaluating OEF through solid waste processing. According to this study, the aerobic biological treatment of MSW is the leading odorous stage in a MBT facility by accounting for an OEF of $1.4 \cdot 10^8$ $OU_E\ t^{-1}$. Other important process steps practiced at the open air, such as curing and storage, were also highlighted as potential odor sources (OEF= 10^6-10^7 $OU_E\ t^{-1}$).

Although they are not widely addressed in the literature, several operational stages of the composting process can be responsible for the release of offensive odors that affect plant workers' warfare and generate odor plumes (Table 5). This is the case of the shredding area of food waste treatment plants where OC can reach values up to 3500 and 6000 $OU_E\ m^{-3}$ (Di et al., 2013; Wu et al., 2015). Likewise, Colón et al. (2017) pointed out that the reception warehouse (storage room) and pretreatment area (sieving unit) were one of the main sources of odor emission in an MBT plant with maximum OC varying from 6000 to 12000 $OU_E\ m^{-3}$. The relevance of waste handling and manipulation on odor nuisance

generation was also stressed by Fischer et al. (2008) who determined the OC of diffused gas emissions generated along the sieving and turning process of a composting pile (Table 5). Notably, this is the only publication performing OC measurements while turning compostable mixtures. ADEME (2012) measured a maximum OC of 1240 OU_E m^{-3} when sampling the passive emissions (area source) produced by the curing process of a pile composed of composted biowastes.

OC and OER inventories published for the handling and post-treatment of anaerobically digested substrates are even fewer than the compilations documented for their odorants emissions (section 4.1.4). In fact, only two research works in the consulted literature performed olfactory measurements along with the storage of digestates (Table 5). Higgins et al. (2006) determined the OC profile when storing anaerobically digested sewage sludge in bottles for 20 days. In this study, OC peaked to 8500 OU_E m^{-3} within the first week of storage, and then began to decrease, following the same trends than methanethiol and DMS emissions. Orzi et al. (2010) evaluated odors emitted by post-digested OFMSW and compared it with emissions from the raw feed-in substrate (ingestate) and the anaerobic digestion unit. According to this investigation, post-digested OFMSW produced higher OER than those measured during the anaerobic treatment (1.4 OU_E s^{-1} and 0.94 OU_E s^{-1}, respectively), whereas there was an apparent reduction of the odor emission potential in comparison with the initial ingestate (4.2 OU_E s^{-1}). As proved by the conducted bibliographic review, there is no existing literature that analyzes and describes the OC and OER profiles during the aerobic treatment of digestates.

To sum up, there is limited information regarding the OC and OER dynamics along the different operational stages of the composting process of various solid wastes and digestates. Also, further research is necessary to enlarge OEF inventories during solid waste processing, particularly through the aerobic treatment (composting active phase) which is frequently seen as the principal odorous step. The main reason for this is that OEF are necessary input data and benchmark values to implement and construct suitable waste treatment facilities and odor control strategies, develop odor dispersion and prediction models, and set up back distances for the construction of new sites. Finally, a large part of the reviewed research works (40%) favored the odor assessment through sensory techniques and left aside the identification of the odor-causing compounds. Combining both approaches is essential to understand the odor generation patterns at composting plants.

4.3. Odor quality (character) and hedonic tone

The odor regulation guidelines actively promote the quantitative assessment of odor impact through OC and OER. Nevertheless, odor quality and hedonic tone are similarly essential odor dimensions that can provide valuable qualitative information about what the perceived odors smell like and their degree of elicited pleasantness or unpleasantness (Leonardos, 1999). In the case of odor quality measurements, common verbal odor descriptors are used to facilitate a constructive dialogue between nearby residents

from waste treatment facilities and plant operators (Decottignies et al., 2013). One of the first attempts to associate odor perceptibility with odor quality and intensity notions was carried out by Leonardos (1999) who outlined that an OC level of 5 OU_E m^{-3} on a composting windrow area (sewage sludge plus wood chips) was reflected into an odor intensity of 1-2.5 (from a nominal scale from 1 to 8), and a rubbery, cabbagy, fishy type odor. Thereafter, Rosenfeld and Suffet (2004) founded the basis to associate the composition of volatile compounds occurring upon composting and their concentrations with the process odor quality through the use of odor detection thresholds. These authors analyzed the gas exhaust from a green waste composting pile and noted that butanoic and valeric acids were likely responsible for the perceived rancid and rotten odors as they accounted for the largest OAV. Based on results from the aforementioned investigation, Rosenfeld et al. (2007) developed a composting odor wheel enabling to associate individual or a set of chemical compounds with their odor signatures and characters (section 2.1.4). This approach was then validated by Suffet et al. (2009) through olfactory tests (odor profile method) in a sewage sludge composting unit. According to this study, biosolids handling and receiving generated odors with predominant fecal, manure, fishy odor notes, while the active composting phase was governed by rancid and rotten vegetable odor characters, typically linked to the anaerobic and aerobic decay of organic matter. Once composted, the odor characters prevailing were earthy-musty and pine notes. These assessed odor characteristics showed a good correspondence with the chemical compounds detected through chemical analysis and those indicated in the composting odor wheel.

The use of the composting odor wheel in odor monitoring has been spread in the last years. Marchand et al. (2013) conducted a Life Cycle Assessment (LCA) to integrate the odor impact in waste management plans by considering some of the substances presented in the composting odor wheel as reference odorants to compute characterization factors. Curren et al. (2016) employed the odor wheel approach to select the appropriate chemical analysis that would identify the odorants perceived by a group of human assessors in a trash transfer station. These authors concluded that MSW odors (in-site) were principally defined by rancid, sulfur, and fragrant characters, while off-site air samples were dominated by sulfur-like odors. Recently, Fisher et al. (2018) designed an odor wheel for wastewater biosolids processing based on results from the olfactory and chemical analysis. In particular, the storage of anaerobically digested sewage sludge was related to sulfur, ammonia/fishy, fecal type odors. It is worth mentioning that edge-cutting technology such as odor detection ports (ODP) coupled to gas chromatography–mass spectrometry (GC/MS-O) has eased the current development of odor wheels because it enables to identify and separate compounds from odorous gas samples and simultaneously evaluate their individual odor characteristics (i.e., quality and intensity) (Barczak et al., 2018; Fisher et al., 2018).

Even if the hedonic tone is a suitable indicator for odor annoyance occurrences (Sucker et al., 2008b), very few reports have characterized and described this odor dimension during solid waste processing. Winter et al. (2004) applied an air-stripping treatment during the storage of biosolid digestate to estimate its impact on the resulting hedonic tone. The un-aerated biosolids produced odors described as

moderately unpleasant (-2 in a nominal scale ranging from -4 to 4) at lower levels of OC exposure (10 OU_E m^{-3}) than the air-stripped biosolids (20 OU_E m^{-3}). Likewise, Higgins et al. (2006) detected a steady decline on the hedonic tone within the first week of biosolid digestate storage, reaching a minimum value of -6 in a scale ranging from 10 (pleasant odors) to -10 (offensive odors). Moreover, high levels of odor annoyances and complaints have been reported in the nearby areas (1.5km<) of large-scale waste treatment units where odors were regularly categorized as unpleasant and significantly strong (Aatamila et al., 2010). Composting plants present different odor sources with different hedonic tones. Chaignaud et al. (2014) analyzed the hedonic tones and OC of gas samples obtained from a green waste pile (used as a bulking agent), a composting cell, and the final compost area. Although these three different odor sources showed similar OC (12000 OU_E m^{-3}), their acceptability level differed considerably. For instance, green wastes exhibited a positive hedonic tone (+4), whereas the composting cell and the final compost area had negative acceptability (-12 and -6, respectively).

5. Problem statement and thesis organization

Odor emissions generated throughout waste treatment affect the comfort, health, and welfare of neighboring residents and plant workers. As a result of odor complaints, several composting plants have closed or presented legal lawsuits. Likewise, odor nuisances cause a negative economic impact on exposed communities by devaluing the price of their properties and lands and decreasing the development of economic activities (i.e., tourism, food trade, etc.) in those areas. Because of the aforementioned drawbacks, odor control and monitoring have become in one of the principal priorities of waste management plans. The first step to face this severe issue is to characterize and understand the odor generation patterns upon waste processing in order to design and implement suitable odor control strategies. Two principal approaches have been employed to characterize odors from environmental gas samples: i) tracing the molecules causing the malodors and ii) assessing the odor impact of emissions through sensory measurement (i.e., odor concentration, odor intensity, hedonic tone). Based on the performed literature review, there are limited studies which conduct complete odor assessments while characterizing odors at the different operational stages of the composting process. In fact, most of the consulted research works have principally focused on evaluating odors and/or odorants during the aerobic treatment of organic matrices since it is generally seen as the primary driver step for odor annoyances. However, the odor and environmental impact of the other process steps such as turning, storage, sieving, and curing have been somehow neglected.

Although some efforts have been previously devoted to analyze the chemical and odor concentration during the composting active phase of some solid wastes (i.e., MSW, sewage sludge, green wastes), published results profoundly differ even for the same type of substrates treated due to the large variation on experimental/operational conditions, waste composition, and the employed analytical/instrumental methodology. Hence, the study of odors upon composting exhibits a lack of systematic characterization

that hinders the inter-comparison among studies at various treatment scales. For instance, more substantial efforts are needed to provide emission factors for the entire sphere of odorous compounds (VOC, VSC, and NH_3). This is also the case for the odor emissions factors (OEF) derived from OC and OER measurements, which despite having a vital role on odor monitoring and control at composting sites, has been evaluated only by one research work. Finally, digestate composting is currently seen as a suitable post-treatment technology to final the biological stabilization of the increasing amount of anaerobically digested substrates produced through the flourishing methanization market; yet, the aside risks of this refining process, such as odor generation and emissions of hazardous compounds, has been barely discussed in the literature.

Linking instrumental-based and sensory measurement has also turned into one of the most investigated topics on odor research. The odor activity value (OAV) approach has shown good results in explaining OC variability; however, some limitations such as the underestimation of predicted values and the lack of reliable ODT have constrained its application. As reported in the literature, the correlation between OC and OAV is far of being fully explored. For instance, no advance multivariate methods such as PLS regression have been used to deeply understand the relationship between sensory measurements and OAV on environmental odor pollution. In the case of the composting process, only one study has evaluated the OC prediction through OAV during the aerobic treatment and storage of pig slaughterhouse sludge. Therefore, there is an urgent need for validating the feasibility of this odor surrogate on predicting OC during the treatment of different organic substrates.

In light of the gaps of knowledge identified above, this thesis has two-fold objectives**: i) to characterize the chemical and odor composition of gas emissions released during the composting process of solid wastes and digestates, and ii) to provide new insight into the relationship between the chemical composition of gas emissions and odor concentration.** It is important to keep in mind that OC prediction based on the chemical composition constitutes only a first stage in the determination of odor nuisances, which could be then more precisely described by relating these parameters to other relevant odor dimensions such hedonic tone, odor quality, and odor intensity.

To achieve the stated general objective, this manuscript was divided into the followings chapters:

Chapter 2: a summary of the employed materials and methods was provided in order to introduce the reader with some methodological aspects no possibly detailed in the scientific articles (due to space limitation).

Chapter 3: a pilot-scale experiment was carried out **to evaluate the patterns of odor generation and odorant composition along the different operational stages of the composting process of anaerobically digested sewage sludge**. In this study, four process stages were simulated: storage,

aerobic treatment by forced aeration (active composting phase), turning and curing. The generated gas emissions were assessed through analytical and sensory methods, enabling to identify the operational stages contributing the most to odor nuisances and recognize the main compounds driving the odor stimuli. The output data from this complete odor assessment was explored in a principal component analysis (PCA) to facilitate the recognition of the odor patterns along the composting process. This research work was submitted to be considered for publication in *Waste Management* under the title: "*Odor generation patterns during different operational composting stages of anaerobically digested sewage sludge*."

Chapter 4: According to the conducted bibliographic analysis, forced aeration treatments of organic matrices have been typically seen as one of the critical steps for odor generation upon composting operations. The odor emission potential of the active composting phase was similarly corroborated in chapter 3. This finding and the reported scientific evidence led us **to characterize extensively the chemical and odor composition of gas emissions released during the forced aerobic treatment of solid waste and digestates under controlled pilot-scale conditions**. In this study, odors were monitored through dynamic olfactometry and instrumental-based methods. The main odor contributors from the gas sample were determined through the OAV approach. To partially limit the impact of using highly variable ODT while computing OAV, 15 ODT were evaluated for the main odorants detected. The characterization of odorous emissions from different substrates composted under the same laboratory conditions allowed establishing inter-comparison among their odor potential and provided reliable emission factors that could be eventually up-scaled, easily compared and used in dispersion models and air pollution control strategies. In this chapter, special attention was paid to evaluate odor emissions factors (OEF) through the aerobic waste treatments as a response to the limited information found in the literature. This research work was published in *Journal of Environmental management* (233 pp. 39-53, 2019) under the title "*Chemical and odor characterization of gas emissions released during composting of solid wastes and digestates."*

Chapter 5: This section was devoted **to analyze the feasibility of instrumental-based measurements (odor activity values) to predict the odor concentration (OC) of emissions released during the aerobic treatment of different organic matrices**. To this end, typical odor surrogates obtained from OAV calculation (OAV_{max} and OAV_{sum}) were correlated to OC by simple linear regressions. To look for new insight into the relationships between OC and OAV, partial least square (PLS) models were developed and consequently compared with the predictability performance of univariate models. The results acquired from the odor monitoring and regression analysis were examined deeply to provide a broader understanding of the origin of odors while composting the organic matrices. This research work was published in *Atmospheric Environment* (222 pp. 1-12, 2019) under the title "*Odor concentration (OC) prediction based on odor activity values (OAV) during composting of solid wastes and digestates."*

Chapter 6: Conclusions and perspectives. In this chapter, the main findings obtained along the conducted experiments were summarized and discussed. The future challenges and perspective to upgrade the knowledge on odors emitted through the composting process were also underlined.

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Chapter 2: Materials and methods

1. Solid wastes and residual organic products (ROP) studied

The first step to meet our objective of enlarging odor and chemical emission inventories during the biological treatment of solid wastes ROP was to select representative organic matrices to be treated and studied. Fifteen organic residues including four anaerobic digestates (AD) were collected at thirteen sites in France throughout a period of 1.5 years. The substrates were classified into five different categories: agricultural wastes, biowastes, green wastes, sewage sludge, and municipal solid wastes. They were sampled at the waste generation source (i.e., farms, green public areas), composting plants (CoP), methanization plants (MeP), wastewater treatment plants (WWTP) and municipal solid waste treatment plants (MSWTP). Table 1 summarizes substrates composition and origins as well as any treatment already applied to samples before they were collected.

Despite having assessed emissions throughout the biological treatment of several organic substrates, there were some relevant solid wastes whose emissions were not evaluated such as the case of cattle manure, fats, and sludge from agro-food industry, among others. Undoubtedly, integrating these wastes to our study design would have provided a broader view of the environmental odor impact of these associated composting activities; however, they would have also increased the sample size drastically in an unmanageable manner. Hence, a more in-depth approach for this type of solid waste or PRO may be necessary for future research works.

Except for the experiment conducted in Chapter 1 aiming at characterizing emissions at different stages of the biological treatment of anaerobically digested sewage sludge (ADS), the composting campaigns were performed in three reactors operating in parallel to treat three different organic substrates. Since compostable materials were collected at various locations in France, it was necessary to store and freeze them previous treatment. Thus, once collected, the substrates were stored at -18 °C in plastic bags and subsequently thawed for two to three days at room temperature before starting the composting experiments.

Table 1. Collected substrates: composition and origins

Type of waste	Substrate[a]	Sampling place[b]	Plant feedstock/substrate composition	Pre-treatment[c]	Acronym
Agricultural wastes	Pig Slurry	Pig farm (CoP)	Solid fraction of pig slurry	Solid-Liquid separation	SPS
	Turkey Manure	Turkey farm (CoP)	Humidified poultry manure	-	TM
	Solid fraction of AD pig slurry	Pig farm (MeP)	Pig slurry (49.6%), food waste (35.5%) and green waste (14.9%)	Wet digestion at 40°C Centrifugation	ADP
Biowastes	Food waste	Restaurant	Fruits and cooked vegetables, meat, pasta, bread, grease, and fish	-	FWR
	Food waste	Restaurant's kitchen	Fruit and vegetable peelings, grease, and coffee ground	-	FWK
	Household food waste from separate collection	CoP	Fruit and vegetable peelings, paper, grease, bread, coffee ground, cooked and raw vegetables, meat, pasta, and bread	-	FWH
	Solid fraction of AD biowaste	MeP	Biowaste of hypermarkets (60%), grease from the food industry (28%), and cereals wastes (12%)	Wet digestion at 40 and 20 °C Screw press	ADB
	Solid fraction of AD biowaste	MeP	Household biowastes (72%), restaurant biowastes (12%), and green biowaste (12%)	Dry digestion at 55°C Screw press	ADH
Green wastes (GW)	Yard trimming	Green area	Leaves, grass, and brush	-	YT
	Green wastes	MeP	Green waste (52%), household biowaste (42%), markets biowaste (2.6%), and restaurant biowastes (2.4%)	Mechanical sorting Mixed and ground	GB
Sewage sludge	Sewage sludge	CoP	Secondary sludge from WWTP	-	SS
	Solid fraction of AD sewage sludge	WWTP	Secondary sludge from WWTP	Wet digestion at 37.5 and 20 °C Centrifugation	ADS
Municipal solid wastes	OFMSW	MSWTP	Food waste, paper, cardboard, sanitary textiles, and plastic films	Pre-fermentation in rotating drums Mechanical sorting	MSW
	OFMSW+ GW	MSWTP	Food waste, paper, cardboard, sanitary textiles, plastic films, and green waste	Pre-fermentation in rotating drums Mechanical sorting	MSG
	Solid fraction of AD OFMSW+GW	MSWTP	Food waste, paper, cardboard, sanitary textiles, plastic films, and green waste	Dry digestion at 40 °C	ADM

[a] AD: anaerobically digested, OFMSW: organic fraction of municipal solid waste, GW: green wastes.
[b] CoP**:** dumping area of composting plants, MeP**:** methanisation plants, WWTP: wastewater treatment plants, MSWTP**:** municipal solid waste treatment plants.
[c] **-:** no pre-treatment.

2. Experimental setup and composting process simulation

The state of the art has shown the complexity and difficulty of characterizing odors and chemical emissions from composting at the industrial scale and receptor areas. The gas exhaust released during the simulation of different operational stages from the biological treatment were analyzed at the laboratory scale (point source) to conduct a systematic characterization of odor emissions for a large set of organic matrices treated under similar and reliable experimental conditions. The laboratory-scale experiments included the simulation of different operational steps, namely, storage, the active phase (forced aeration), turning process, and curing. Some process such as the solid-liquid separation of digestates and sieving of the compostable mixture to separate final compost from the bulking agent were not addressed in this research work.

Gas emissions released during different operational composting stages were characterized on a single waste, ADS (Chapter 3), whereas the gas exhausts generated upon forced aeration treatments (active phase) were assessed for the fifteen residues mentioned in Table 1 (Chapter 4).

2.1. Storage simulation

The storage phase was simulated in a reactor consisting of a cylindrical stainless steel tank (volume= 270 L, height= 0.93 m and diameter= 0.69 m) insulated with a layer of polyurethane (thickness= 10 cm). The reactor had a stainless steel grid where the collected organic matrices were placed. Once loaded, the storage device was sealed by a metallic conic-shaped cover that contained gas outlets and a gutter to collect possible condensates formed through the storage process. Condensates were collected outside the reactor. The storage device was also equipped with a closed outlet located at the reactor's bottom to extract any produced leachate. The pilot was placed on three mass sensors enabling to track and register variations on substrates' weight. Also, temperature probes were inserted in the composting pilot to monitor temperature variations continuously. These temperature probes were located in the gas headspace above the compostable material.

The storage phase was simulated for seven days by placing the target organic substrate into the reactor, without the addition of a bulking agent, and applying a sweeping airflow on the material's surface. The air inflow was supplied by a regulated air compressor. The sweeping air flow rate was controlled and monitored by a flow meter and gas meter. The applied airflow rate was equal to 0.15 m^3 h^{-1} m^{-2} reactor area. The temperature, hygrometry, pressure, as well as the O_2, CO_2, CH_4 and N_2O concentrations for the incoming and outgoing gas stream, were measured in continuous. The measured values were acquired online by a central acquisition unit Agilent 34 970A and its associated software (Benchlink Data Logger).

A second water condenser (5 L) was used to collect any water excess present in the reactor's gas exhaust. A part of the gas out stream was conveyed toward a set of gas scrubbers containing an acidic solution of H_2SO_4 (4%) to trap and quantify ammonia. Gas samples were also collected to assess the odor concentration, and chemical composition of the channeled outflows, once they crossed the second condensate traps. The experimental storage device is shown in Fig. 1.

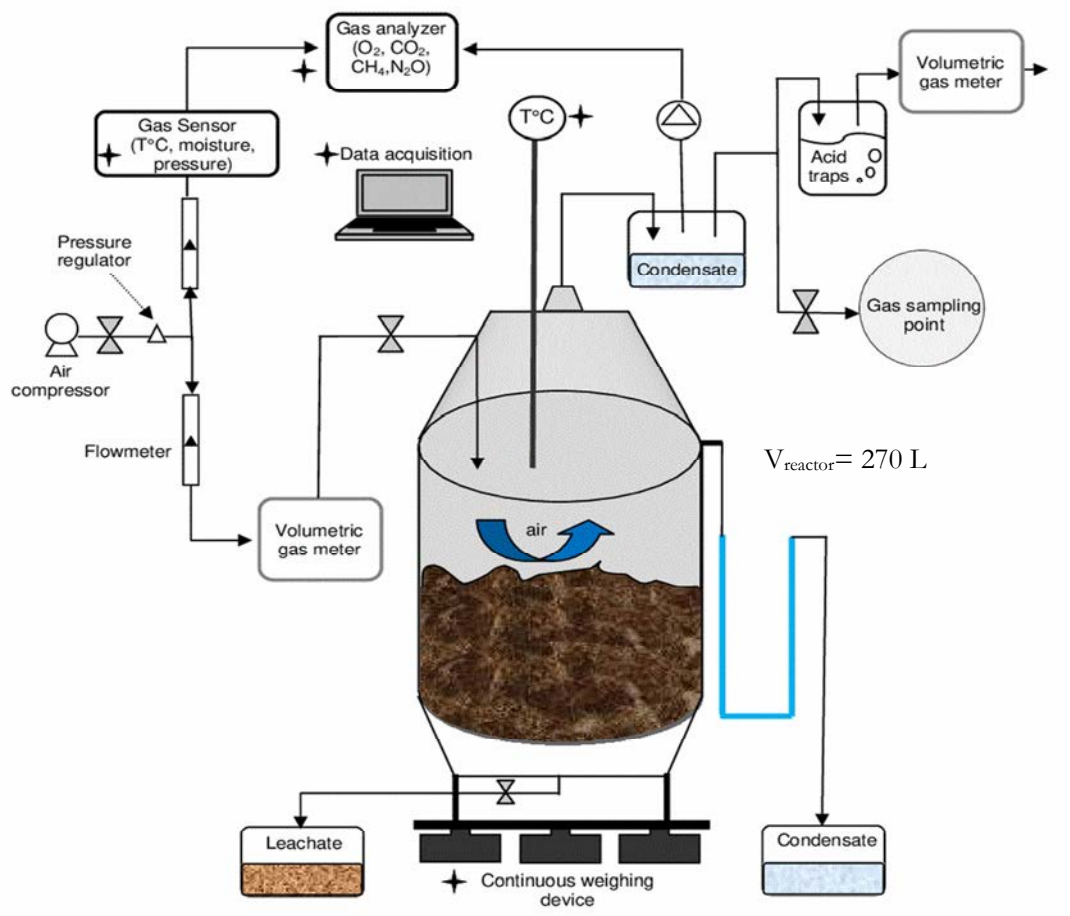


Fig. 1. Experimental device used to simulate and monitor gas emissions during storage and curing stage

2.2. Simulation and monitoring of the composting active phase

The experimental device used to simulate and monitor the active phase (Fig. 2) was relatively similar to the one implemented upon storage. The principal differences between both setups were that i) the active phase was conducted and monitored for 4 to 5 weeks, ii) the solid wastes or ROP were often mixed with a bulking agent before being load in the reactor, and iii) the application of a forced aeration treatment by injecting an upward airflow into the composting pile. The air inlet was located at the reactor's bottom to warrant that the air flow crosses the treated organic matrices evenly to be then evacuated through the gas outlet found on the upper lid.

Wood chips were added as a bulking agent while conducting the forced aerobic treatments of some studied solid wastes and ROP. The mixing process of the bulking agent and substrates was carried out in a concrete mixer. The mixing ratio bulking agent to substrates (BA/S) and aeration rates applied were established according to i) the conditions applied by the platforms treating the sampled substrates and ii) previous studies performed at Irstea concerning the influence of composting conditions on odor emissions and waste biodegradability (Blazy et al., 2014; de Guardia et al., 2010). A low aeration rate was initially applied the first 24 to 48 hours after loading the reactors, followed by an increased on aeration rates to values that were kept constant until the end of the forced aeration treatments.

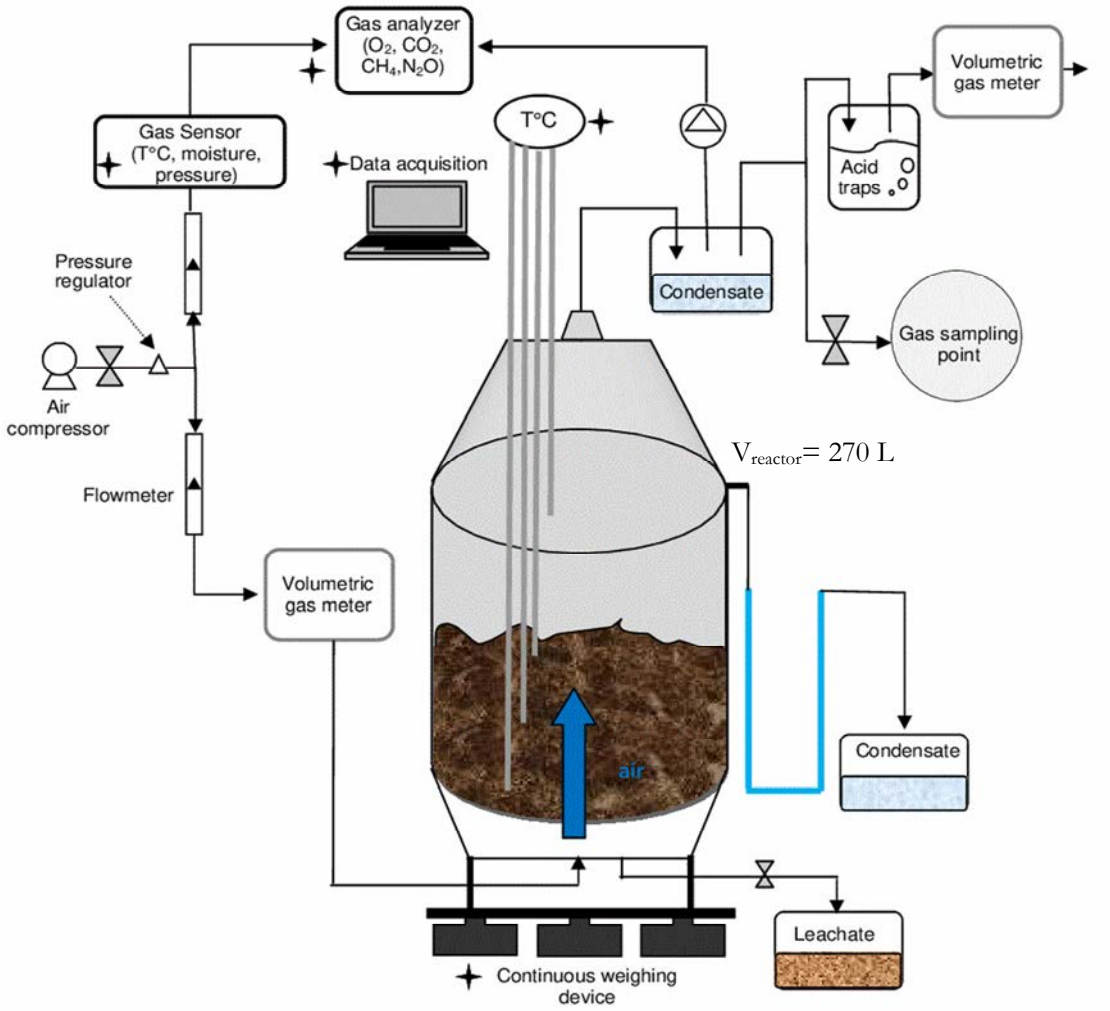


Fig. 2. Experimental device used to simulate and monitor the composting active phase

2.3. Simulation of the turning process

During the active phase, two turning processes were simulated by emptying the composting reactor content and mixing the treated substrate manually. Generally, at industrial scale, turning procedure can be carried out from one to four or five times depending on the treated substrate. Four samples of approximately 7-8 kg were collected throughout the discharge process by sampling material located at

different heights of the composting pile (i.e., bottom, middle and top sections). The obtained samples were then placed in 4 plastic containers (Volume= 30 L) connected in series and sealed with tight covers containing air inlets and outlets. An air inflow was initially applied at the inlet of the first plastic container to generate a sweeping surface airflow that crossed all four buckets. The resulting gas outflow was then transferred towards an acid trap capturing ammonia and a gas sampling point. Volumetric gas meters were connected to the first air inlet and the acid trap system to measure and control flows. Finally, the turning procedure was simulated by stirring the four containers simultaneously. The aeration rates used through the turning simulations were 45 and 60 L h^{-1} kg^{-1} WB (wet basis) in order to approach to real operational conditions where turning pile is conducted at open air and it is therefore more exposed to ambient airflow. The gaseous emissions were monitored for 2h and 3h20min, respectively to see the effect of turning the pile on odor and chemical emissions. Hanajima et al. (2010) demonstrated that turning a composting pile triggered the release of odor-causing emissions for the next hours after conducting the mixture of compostable material.

After being turned, all compostable material was reintroduced to the composting pilots to continue the forced aeration treatments. The experimental device employed to simulate the turning process and monitor its gas emissions is depicted in Fig. 3.

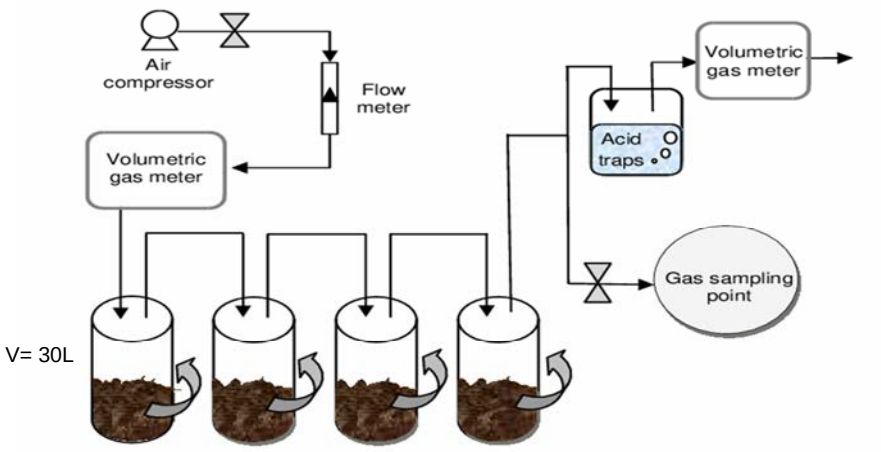


Fig. 3. Experimental device used to monitor gas emissions during the turning of compostable substrates

2.4. Simulation of the curing process

The active phase is characterized by an intense stabilization of organic matter through the aerobic biodegradation process which is reflected in significant levels of oxygen consumption and microbial activity. After fulfilling such extensive oxygen demand, the material biodegradability slows down, and a curing stage starts. In this stage, the organic matter is mainly reorganized, and a forced aeration treatment is not needed. Curing can be performed whether in the presence or absence of bulking agent by sieving

the compostable mixture obtained at the end of the active phase. In this study, the curing process of ADS was performed without sieving the compostable mixture because of the low biodegradability and high bulk density (considerable material compaction) of the studied substrate. The presence of the bulking agent inside the cured pile triggered the establishment of aerobic conditions and heat accumulation.

The experimental device used to simulate and monitor the curing process is identical to the one described upon storage (Fig. 1). Yet, the curing phase was conducted and evaluated for four weeks.

3. Sampling and characterization of gas emissions

3.1. Gas sampling

Gas samples were collected under room conditions at the outlet of the experimental devices used to simulate the composting process. In the case of the forced aeration treatment, storage and curing, the channeled outward flow first crossed a 5 L glass bottle at room temperature to condense any excess of water that may interfere while conducting the sensory and analytical measurements. For the turning process simulation, samples were directly taken at the device's outlet. The gas sampling process was carried out through the use of home-made nalophan® gasbags (V= 30 L) previously preconditioned by flushing them with analytical grade air (three times). The single-use gas sampling bags were filled automatically in 10 to 30 minutes by the channeled out airstreams according to the NF EN 13725 guidelines for point sources (AFNOR, 2003). Gas sampling was conducted two or three times per week during the composting simulations by collecting three or two replicates per day under the same conditions and time. Special attention was paid to perform punctual gas sampling after removing water condensates in the glass bottle (water trap), thus avoiding possible dilution and loss of hydrophilic compounds. Thereafter, gas samples were shortly analyzed or processed within 1 to 6 hours after being sampled to minimize the impact of gas sample storage on compounds and odor losses. Some authors have recommended limiting gas samples storage to 6h (Mochalski et al., 2009; Van Harreveld, 2003).

3.2. Odor and chemical characterization

Based on the conducted literature review, relatively few studies confront and analyze both, the chemical composition and odor sensory properties of gas emissions released during the composting process. In this research work, we attempted to address both dimensions of odor pollution by employing a broad range of analytical and sensory methods.

3.2.1. Analytical methods

Chemical analysis using instrumental-based methods were employed to analyze the principal families of odorants released upon composting according to the literature, namely, ammonia, volatile organic compounds (VOC) and volatile sulfur compounds (VSC).

3.2.1.1. Ammonia

Ammonia was analyzed directly at the channeled outflow of the experimental devices through an acid traps system. To this end, two serial glass impingers containing acid solutions of H_2SO_4 (1 N) were connected to the reactors outlet. Acid traps were changed every time gas samples were collected for chemical and olfactometric characterization in order to avoid the saturation of acid solutions with ammonia. The outflow passing through the acid trap system was continuously monitored and controlled by a flow meter and volumetric gas counter. Finally, adsorbed ammonia was released through steam distillation and quantified by back-titration with H_2SO_4 (0.2 N) according to the modified method NF T90-015-1 (NF T90-015-1, 2000).

3.2.1.2. Volatile organic compounds (VOC)

The gas samples collected in nalophan bags at the reactors' outlets were analyzed by a GC/MS (Clarus 500 GC-MS, Perkin Elmer, USA) coupled to a thermal desorption unit (TurboMatrix 550, Perkin Elmer, TD-GC/MS).

A pre-concentration step was first applied to trap VOC onto sorbent tubes (Carbotraps 349, Perkin Elmer, USA) at different concentration levels. A calibrated vacuum pump (Gilair3, USA) functioning in a negative pressure mode at a flow rate of approximately 50 mL min^{-1} was used to adsorb different volumes of the gas sample onto the carbotraps (i.e., 50, 250, and 500 mL). Sorbent tubes were stored at 4 °C for 1 to 2 weeks before being analyzed by GC/MS.

Once pre-concentrated, VOC were desorbed by a thermal desorption unit at 200 °C for 5 min (primary desorption) and conveyed into an inner cold trap (T= 5 °C) through a nitrogen (N_2) flow of 50 mL min^{-1}. A secondary thermal desorption was then applied at 180 °C for 5 min to release trapped VOC in the inner cold trap. The desorbed VOC were transferred toward a GC/MS (Clarus 500 GC-MS, Perkin Elmer, USA) where they were eluted and separated into a capillary column CP- WAX 58 (25m×0.15mm x 0.25 µm, Varian, USA) using helium (1 mL min^{-1}) as a carrier gas. The oven GC temperature program consisted of an initial oven temperature of 40 °C held for 5 min, followed by a temperature ramp to 180 °C at 10 °C min^{-1}. This final oven temperature was maintained for 5 min.

Each VOC separated at different retention times were scanned into a quadrupole mass spectrometer detector acquiring from 20 to 300 amu (atomic mass unit) every 1.5 s. Two principal criteria were used to identify the separated compounds: i) the match percentage of the obtained mass spectra with the reference entries from the spectral mass library NIST (National Institute of Standards and Technology, USA) and ii) the comparison between the retention times of the resolved analytes with the ones obtained when analyzing chemical standards. Two acquisition modes were employed to analyze the resulting chromatograms and integrate peaks areas: i) a full scan mode showing all scanned ions in the selected mass range. This scan mode was initially used to identify the VOC present in the gas samples and the mass to charge ratio (m/z) of their diagnostic ions (the ion presenting the highest abundance); ii) a single ion monitoring (SIM) mode to trace and quantify the substances of interest presenting specific mass to charge ratios. SIM mode allowed excluding irrelevant masses and improved the acquisition sensibility. Indeed, peak area integration was generally conducted in a SIM mode.

The identified analytes were quantified by relating their integrated areas to response coefficients obtained through external calibration. To conduct this external calibration, a defined amount of chemical standards with high purity (Purity > 98%) were injected into an airtight glass flask containing 10 L of air. The diluted compounds at known concentration were then adsorbed onto sorbent tubes at different volumes and mass quantities to set a calibration range (i.e., 400-800-1200-1600 ng). Prepared carbotraps were finally analyzed by TD-GC/MS following the methodology described above. The calibration curve and the response coefficient (slope, i.e., unit area ng^{-1}) were yielded by associating the standard mass quantities with the generated unit area responses.

The gas emissions released during composting are characterized for containing a large variety of volatile compounds, making it impossible to quantify all of them. Hence, special priority was given to measure and calibrate odorous compounds presenting low ODT. Not calibrated compounds were semi-quantified by taking into account the average coefficient responses from the performed calibration sessions (i.e., 1000 and 630). The method detection limits (MDL) was determined by linear extrapolation of the minimum standard quantity required to have a ratio signal to noise equal to 3, whereas the limit of quantification was calculated by considering a ratio signal to noise equal to 9 (Defoer et al., 2002; Mochalski et al., 2009).

3.2.1.3. Volatile sulfur compounds (VSC)

TD-GC/MS is a powerful tool to determine a vast spectrum of VOC. However, sulfur-containing compounds are thermally unstable and can be oxidized when they are exposed to the high temperatures commonly employed during thermal desorption, which may lead to the formation of artifacts and dimers (i.e., CH_3SH may be oxidized to CH_3SCH_3)(Blazy et al., 2015; Muñoz et al., 2010). Therefore, a gas

chromatographer coupled to electrochemical detection (airMEDOR, Chromatotec, France) was employed to assesses VSC according to the ISO 6326-2 (1981) guidelines. This gas chromatographer was specifically designed to analyze both, inorganic and organic sulfur-containing molecules, using relatively low operational temperatures. The target analytes were hydrogen sulfide (H_2S), dimethyl disulfide (DMDS), dimethyl sulfide (DMS), methanethiol (CH_3SH) and ethanethiol (CH_3CH_2SH).

The VSC analysis consisted of pumping the collected gas samples in nalophan bags toward a 400 µL loop injection valve at a flow rate of 100 mL min^{-1}. The gas trapped inside the loop valve was then injected into a capillary column (1.2 m×1.6 mm x 180 µm) held at 40 °C and eluted using air as carrier gas at a flow of 4 mL min^{-1}. The column pressure was kept at 230 hPa throughout the analysis. Once separated, VSC were detected by an electrochemical cell containing two platinum electrodes placed into a chromic oxide solution (CrO_3, 10% w). The eluted VSC underwent REDOX reactions and generated electric potential differences that were measured and recorded as unit areas at different retention times. The resolved VSC were quantified through external calibration and internal calibration. To this end, pure chemical standards (DMDS, DMS, and ethanethiol) or standard gases (CH_3SH and H_2S) were diluted with analytical grade air at different concentrations (i.e., 0.1-1-2-5 mg m^{-3}) in nalophan bags to be analyzed following the procedure described above. The method detection limits (MDL) were calculated by extrapolating the minimum area measured by MEDOR (1000 units area) into the performed calibration curves. A permeation tube was also used to calibrate the equipment for DMS.

3.2.2. Sensory methods and odor monitoring

Odor concentration (OC) is undoubtedly the odor sensory property more widely assessed and employed within the odor regulatory framework at waste treatment units. This approach can be combined with chemical analysis to provide broader insight into odor nuisance potential of gas emissions from composting process, notably, through the use of odor detection thresholds of identified volatile compounds and the calculation of odor activity values (OAV).

3.2.2.1. Odor concentration (OC) and odor emission rates (OER) measurement

Odor concentration in European odor units (OU_E m^{-3}) was measured through dynamic olfactometry following the FR EN 13725 guidelines (AFNOR, 2003). In this method, the gas samples collected from the reactors' outlets were diluted by mixing known flows of polluted air (sample) and neutral gas (medical grade air) at defined ratios and consequently presented to a group of assessors. The odor concentration was computed based on the dilution factor in which half of the calibrated human panel perceived an odor stimulus (odor detection threshold) under standard dynamic olfactometry conditions.

A dynamic olfactometer ONOSE 8 (Consumaj, Canada) was employed to perform and present the dilutions of the tested gas samples automatically. Onose 8 was constructed according to the criteria established by EN 13725. For instance, the olfactometer's components are made of Teflon®, stainless steel or glass. The dilution apparatus was placed in an air-conditioned room with a slight overpressure where the temperature and the renewal of the indoor air were controlled. Also, the dilution system accounts for precise mass flow controllers with a reading error ranging from 0.1 to 1 %. To conduct OC measurement, the gas sample was first adsorbed by a negative pressure line (vacuum) toward a supply plenum containing the polluted air. This collected gas sample was then mixed with analytical grade air in a second air chamber and delivered toward a three-port sniffing station. Before being mixed and delivered, compressed air was treated by an active carbon filter to remove any trace of odorous compounds. The opening and closing of solenoid valves in the apparatus' fluid system determined the airflow lines taken by the polluted and clean air. Only one of the three sniffing ports delivered the diluted gas sample, while the other two ports were supplied with clean air (Fig. 4A). The sniffing port delivering the diluted gas sample was chosen randomly by an algorithm. The olfactometer includes eight panelist positions and an operator position.

Before carrying out the olfactometric tests, an odor panel were screened and selected based on their sensibility to n-butanol. According to EN 13725, one European odor unit (OU_E) is exerted by 123 μg m^{-3} n-butanol. Hence, odor assessors were expected to account for an odor detection threshold to n-butanol that fall in a range from 62 to 246 μg m^{-3}; that is between 0.5 to 2 times the expected value when evaluating the reference material. Several calibration sessions were performed before, during and after the experimental campaigns in order to screen regularly the odor assessors. Gas samples used for calibration purposes were prepared by injecting a known volume of n-butanol (Sigma-Aldrich 99.9%) into home-made nalophan bags filled with a defined volume of clean air. A total of 15 panelists were recruited and trained; however, between five up to eight assessors were convened to attend per olfactometry session (Fig. 4B).

For extremely high odorous emissions, gas samples were pre-diluted 100 folds by using a tight gas syringe (SGE, Australia). The olfactometric tests of collected gases or pre-diluted samples began by diluting the sample with clean air to levels not perceivable by assessors. Thereafter, the tested gas samples were presented to the assessors in an ascending concentration order by reducing the dilution rates in a step factor of two to reach a dilution level where all panelists could perceive an odor stimulus. ONOSE 8 enabled to deliver accurate dilutions within a dilution range varying from 6.5 to 53333 ($2^{2.7}$-$2^{15.7}$) in a stabilization time of 10s. Each dilution presentation, from no odor stimuli to odor detection, was assessed by the odor panel to determine the dilution factor at the 50% of odor detection threshold (Z_{50}). The odor detectability of panelist was evaluated in a forced-choice mode involving the identification of an odor stimulus from odorless gas in the three-port sniffing station (Fig.4A). To this end, two questions were asked to assessors: i) can you perceive an odor (yes or not)? ii) If yes, in which port do you detect it (port

A, B, or C)? All responses were registered and treated in real time by the olfactometer's software (Olfaware).

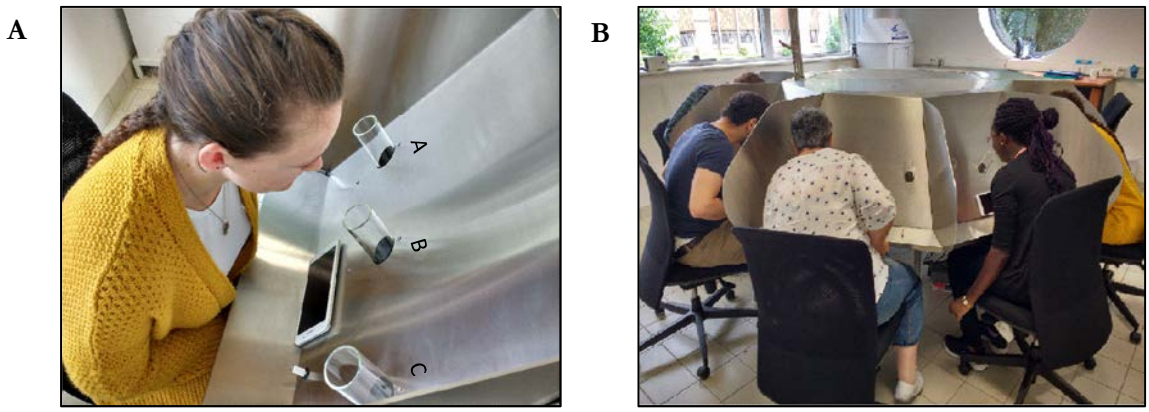
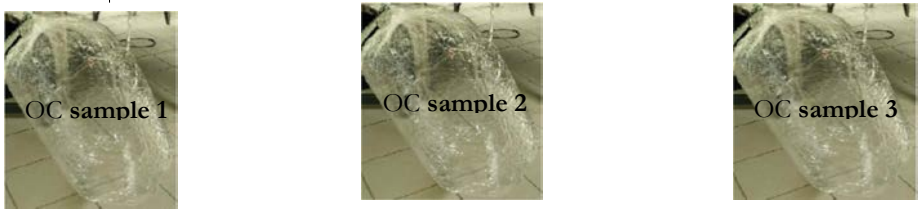


Fig. 4. Dynamic olfactometer and odor concentration (OC) measurement: three port-sniffing station (**A**), odor panel formed by 5 up to 8 assessors (**B**)

The Z_{50} of each gas sample was measured in three different rounds. The first round was always discarded. However, the measured individual threshold estimates (Z_{ITE}) from each panelist during the second and third rounds were taken into account to calculate the Z_{50} geometric mean of the entire panel, which is equivalent to OC under standard conditions. Furthermore, results from duplicates or triplicates at each sampling day were averaged to yield a final OC geometric mean. The OC determination procedure is summarized in Fig. 5.

	Odor panel				
Olfactory test	Assessor 1	Assessor 2	Assessor 3	Assessor 4	Assessor 5
Round 1	Not considered				
Round 2	Z_{ITE1-2}	Z_{ITE2-2}	Z_{ITE3-2}	Z_{ITE4-2}	Z_{ITE5-2}
Round 3	Z_{ITE1-3}	Z_{ITE2-3}	Z_{ITE3-3}	Z_{ITE4-3}	Z_{ITE5-3}
Av. Z_{ITE} (Geometric mean of Z_{ITE})	Av. Z_{ITE-1}	Av. Z_{ITE-2}	Av. Z_{ITE-3}	Av. Z_{ITE-4}	Av. Z_{ITE-5}
Z_{50}=OC **sample 1**	Geometric mean of Z_{ITE} from the entire panel (Av. $Z_{ITE.panel}$)				



OC_{final}= Geometric mean of OC from replicates

Fig. 5. Determination of the odor concentration (OC in OU_E m^{-3}) during a dynamic olfactometry session. Z_{ITE} is the individual detection threshold of a specific assessor at each tested round (Adapted from Blazy, 2014)

Once OC was measured, the odor emissions rates (OER in $OU_E\ h^{-1}$) were yielded by multiplying the determined odor concentrations ($OU_E\ m^{-3}$) by the outflows ($m^3\ h^{-1}$) at the outlet of the composting simulation devices. OER was expressed as a function of the initial organic matter content (OM_0) of the substrates composted ($OU_E\ h^{-1}\ kgOM_0$). Furthermore, odor emission factors (OEF in $OU_E\ g\ OM_0$) were determined for all studied operational composting stages by integrating OER during the operational stages duration (cumulative OC).

The EN 13725 guidelines establish a 95% confidence interval of OC measurements based on the number of replicates analyzed during the olfactometry test. The 95% confidence interval of odor concentration (OC_{int}) was computed by Eq. 1.

$$OC - t * \frac{S_r}{\sqrt{n}} \leq m \leq OC + t * \frac{S_r}{\sqrt{n}} \quad \text{Eq. 1}$$

Where m is the expected values of the test results, OC is the geometric mean of odor concentration (OC_{final}) logarithmically transformed; *t* is the Student's t-factor (t=2 for a confidence interval of 95%), Sr is the standard deviation from laboratory repeatability (0.1721, defined by the norm according to the expected precision criterion), and n is the number of replicates assessed (n). The average number of replicates evaluated along the composting campaigns was 2.5, thus leading to obtain the following 95% confidence interval for the performed OC measurements (Eq.2):

$$OC - 0.22 \leq m \leq OC + 0.22 \quad \text{Eq. 2}$$

3.2.2.2. Odor detection thresholds (ODT) of pure substances

Monitoring odors through the identification of the odor-causing compounds involve the comparison of the substances' concentration levels with their reported or measured ODT. Despite its importance in odor regulation, this approach is hindered by the considerable variability on ODT datasets (Parker et al., 2012). In this research work, the ODT for 15 pure substances was determined by the same trained odor panel that evaluated the gas samples collected upon composting. The measured ODT included some of the most frequently detected and odorous compounds such as VSC and trimethylamine (see Chapters 4 and 5). The ODT measurements were conducted using the same methodology based on EN 13725 previously described in section 3.2.2.1. However, the principal difference is that ODT measurement was carried out using nalophan bags that contained one single compound. The tested gas samples were prepared in replicates by injecting pure chemical standard or gas standards into nalophan bags filled with a known volume of analytical grade air. The theoretical compound concentrations were computed as the ratio of the mass injected into the final gas sample volume and ranged from 0.4 to 404 mg m^{-3}.

The odor panel assessed the dilution factor at 50% detection threshold within one to three hours after the gas samples preparation. Some studies have reported compounds and odor losses due to gas sampling storage in nalophan bags which could lead to the reduction of the calculated theoretical concentration. Hence, the exposure chemical concentration (C_0 in mg m^{-3}) at the time of the olfactory experiments for a maximum storage time (3h) was estimated by considering the measured losses of compounds in nalophan bags through GC/MS and MEDOR, but also based on previous reports on compounds recoveries in nalophan bags (Hansen et al., 2012; Sironi et al., 2014). The ODT of a tested compound (ODT_i) was yielded by relating the compound's exposure concentration to the measured dilution factor at 50% detection threshold as shown in Eq. 3:

$$ODT_i = \frac{C_0}{Z_{50}} \quad \text{Eq. 3}$$

3.2.2.3. Odor activity values (OAV)

The odor activity value (OAV) is a dimensionless parameter commonly employed in odor assessments to trace and identify the volatile compounds of a gas mixture that contribute actively to odor nuisances (Rincón et al., 2019). This term was calculated for a large part of the substances identified and quantified along the chemical analysis using Eq. 4:

$$OAV_i = \frac{C_i}{ODT_i} \quad \text{Eq. 4}$$

Where OAV_i is the odor activity value of a specific substance contained in the gas sample, C_i is the chemical concentration detected through instrumental-based methods (section 3.2.1), and ODT_i is the measured or reported odor detection threshold (ODT_i) for that substance. Notably, the ODT determined through dynamic olfactometry were preferably used to calculate OAV. For some substances, ODT were not assessed and then consulted in reported ODT datasets (Nagata, 2003 and Van Gemert, 2011). It should be mentioned that ODT for certain molecules were not found in the literature (i.e., 7 compounds in Chapter 4), thus leading to underestimate their odor potential in the released and analyzed emissions. Once computed, individual OAV of compounds present in the collected gas mixtures were used to yield two common odor surrogates derived from OAV calculation: i) OAV_{max}, defined as the highest OAV detected within the gas mixture, and ii) OAV_{sum}, yielded by adding the OAV of all quantified and assessed compounds.

4. Data analysis: statistical approaches

4.1. Principal component analysis (PCA)

A PCA was conducted on the acquired datasets from OAV calculation and OC measurement throughout the different operational stages of ADS composting (Chapter 3) by The Unscrambler X version 10.5 (CAMO, 2018). The principal aim at using this data mining approach was to discover and ease the recognition of relevant odor patterns while composting ADS. By definition, PCA is an unsupervised technique (or exploratory method) that allows visualizing all the information or variation contained in a data table (matrix) more simply, as well as quantify and identify the amount of useful information and meaningless variation present in that data (CAMO, 2006). To do so, a one-block data matrix (X) is decomposed into a new set of orthogonal variables called Principal Components (PC, Fig. 6), which are linear combinations of the initial variables in a multidimensional space (Toledo et al., 2018). These linear combinations or directions are the outer products of two vectors (X= TP'+E) called loadings (projection of the columns-P') and scores (projection of the rows-T) which are determined pair-by-pair in an iterative procedure such as the nonlinear iterative partial least square (NIPALS) algorithm (Geladi and Kowalski, 1986).

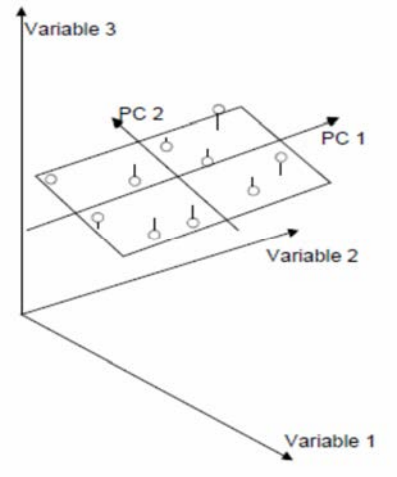


Fig. 6. Principal Components (PC) in a multidimensional space (Camo, 2006)

The major gain of using this new set of coordinate axes (Principal Components) is that they are orthogonal and ranked. As a result of these properties, the first Principal Components (i.e., PC_1 and PC_2) will explain a large part of the matrix information (variance), making possible to prioritize and target the most relevant information with the final aim at establishing interpretations about the data's patterns and structure.

In Chapter 3, a one-block matrix (X) was used to carry out the PCA. This matrix was constituted by two variables (columns): the OAV of volatile compounds (19 substance) and OC measurements. Such variables were determined for all collected and analyzed gas samples (rows) through the different composting operational stages of ADS. A summary of the data matrix is shown in Fig. 7.

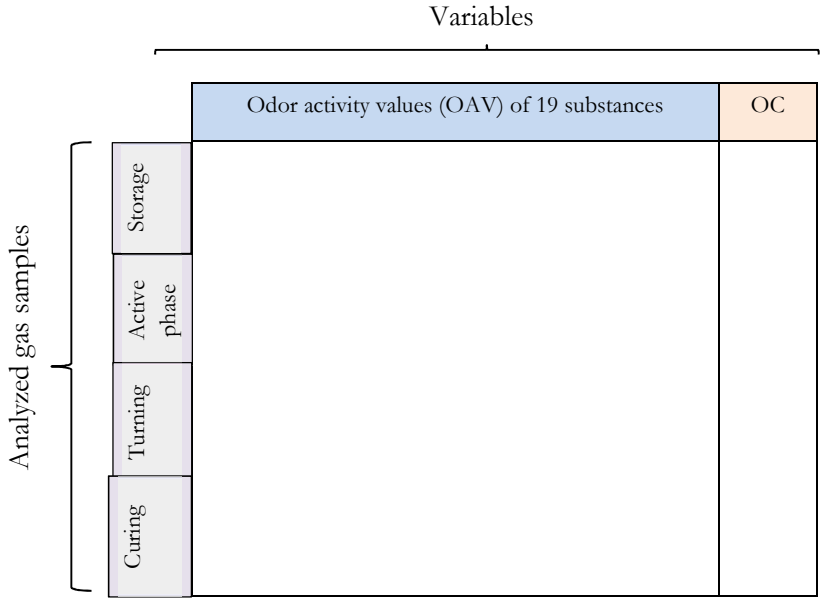


Fig. 7. One-block data matrix (X) employed to evaluate odor patterns along the composting process of ADS (Chapter 3)

Before conducting the multivariate analysis, OC and OAV were logarithmically transformed to reach normal data distribution. This scaling process limited background noises caused by irrelevant variation and highlighted correlation patterns among variables. Furthermore, the matrix's missing values caused by non-detected values of compounds were substituted by half of their detection limits to perform the statistical treatments of data (Blanes-Vidal et al., 2009; Susaya et al., 2011). The outcomes from the PCA on X were plotted in two graphs: the scores plot and correlation loadings plot. The score plot describes the location of the gas samples in each model component, thus enabling to determine samples patterns, clusters, but also detect outliers (data points not fitting into the general patterns)(Toledo et al., 2018). For instance, one outlier was identified and discarded during the first turning process of ADS. On the other hand, the correlation loadings plot allows determining how much the initial variables contribute to the data variance explanation on the model components (high loadings close to +1 or -1 are translated into high contributions), as well as tracing possible correlations among variables and gas samples according to their position in the multidimensional space (close variables are highly correlated) (Toledo et al., 2018).

4.2. Univariate and multivariate correlations

As a consequence of stricter odor regulations and the high cost of sensory tests, there is a growing interest in seeking OC predictors that can assist odor surveys in the absence of olfactometry analysis. OAV approach has shown good performance in predicting OC for some defined odor sources with certain reported uncertainties and shortcomings. Therefore, the relationship between OAV and OC is far of being fully explored, particularly during the composting process of different organic matrices. In Chapter 5, we explored univariate and multivariate regression analysis to study the link between OAV and OC while aerobically treating nine solid waste and digestates.

4.2.1. Simple linear regressions

Firstly, the feasibility of OAV to predict OC was straightforwardly assessed through simple linear regression models. To this end, two odor surrogates derived from OAV calculation (OAV_{max} and OAV_{sum}, section 3.2.2.3) were linearly regressed against OC. Since both variables, OC and OAV, are log-normally distributed, they were logarithmically transformed before carrying out the correlation analysis (Hansen et al., 2016). The regression lines were forced to pass through the origin by assuming that OC is proportional to OAV. Hence, two simple linear model were tested: i) Log (OAV_{max}) = βLog (OC) and ii) Log (OAV_{sum}) = βLog (OC). Using XLSTAT (Addinsoft, 2018), the coefficients of determination (R^2) were determined to evaluate how well the simple linear regression models predicted the measured OC (goodness of fit), as well as the closeness of the predicted values in regards to the 95 % confidence interval set for dynamic olfactometry (EN 13725).

4.2.2. Partial least square (PLS) regressions

The PLS regression, also called projection of the latent structures, is a powerful multivariable linear model enabling to relate two-block data matrices X (independent) and Y (dependent) under situations where other typical multivariable methods (i.e., multivariate linear regression-MLR) do not work. For instance, when the matrices present highly co-linear and noisy variables, or the number of variables is superior to the number of samples (Biasioli et al., 2004). In this method, X and Y matrices are modeled simultaneously to encounter projected latent variables (PLS components) in X that will accurately explain and predict the projected latent variables in Y (Camo, 2006). To obtain PLS components, it is necessary to set outer relations (block X and Y individually) and an inner relation linking both matrices (Geladi and Kowalski, 1986). The outer relations are obtained by describing each matrix block as Principal Components (PC) consisting of scores and loadings, as follows:

i) $X = T^{*}P' + E$

ii) $Y = U^{*}Q + F$

Where T and U are the scores for X and Y matrices, respectively, P and Q are the loadings for both matrices, and E and F are the associated residuals. These external relations are conducted simultaneously in order to find the most suitable inner relation between X and Y. To search for this inner relation, the Y scores blocks (u) are related to the score blocks of X (t) for every PLS component through an iterative procedure such as the NIPALS algorithm. The resulting inner relation has the form u = b*t, where b plays the role of regression coefficients (Geladi and Kowalski, 1986). Therefore, the heart of the PLS analysis is to find PLS components where "u scores values" have the maximum covariance with "t scores values," and their associated residuals are minimized. The procedure to construct PLS components is summarized in Fig. 8.

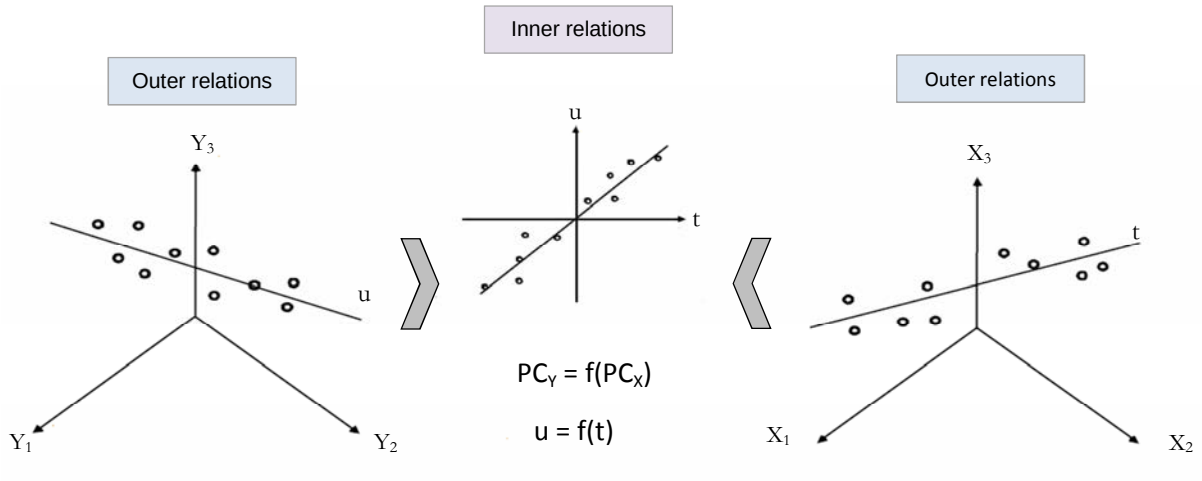


Fig. 8. Basic procedure to construct PLS components (Adapted from Camo, 2006)

In Chapter 5, PLS1 models were developed to predict OC (one dependent variable-Y) based on OAV from 22 quantified analytes (explanatory or independent variables). The starting matrix used to elaborate the PLS regressions was similar to the one used upon PCA (Fig. 6); however, for this particular case, OC column was considered as a dependent matrix (Y), and gas samples were obtained and analyzed during the composting active phase of different organic substrates.

Before constructing the PLS models, the X- and Y- variables were scaled. Again, using a logarithmic scale was found to be a suitable approach because OC and OAV data were spread over several orders (skewed distribution), and due to the non-linear nature of odors, commonly described through a power law (Biasioli et al., 2004; Hansen et al., 2016). Once the variables were scaled, the initial matrices were divided into a training set and a test set. Both datasets contained representative information (samples) about the odorous gas emissions collected along the aerobic treatment of diverse organic substrates. The

training set was employed to construct the PLS calibration models and obtain the models' parameters (i.e., regression coefficients). Contrarily, the test set consisted of a subgroup of measured samples (OAV and OC are known) not used during the model construction, which were consequently fed into the calibrated model to predict the dependent variable ($OC_{predicted}$). These predicted values were finally confronted with the observed Y values ($OC_{measured}$) to validate and assess the predictive ability of the calibrated models. The predicted and observed Y values were compared to yield the coefficient of determination for prediction (R^2_{pred}), the prediction residuals and the root mean square error of prediction (RMSEP). This later term measured the average uncertainty when predicting OC from new samples, and it was expressed in the same units than Y ($OU_E\ m^{-3}$). During the models' construction, special care was taken to develop a final calibration model that exhibited the lowest RMSEP and residual variance as possible.

Besides performing test set validation, a cross validation process was applied to assess the predictive significance of the calibrated models and identify non-significant variables through the so-called jack-knifing approach. Notably, segmented cross validation was adopted by dividing the training set into 20 different segments chosen randomly by the software. Such cross validation (CV) process consisted of leaving one segment of samples at a time to obtain a sub-model that were tested on those samples keeping out. Hence, the OC of left-out samples were predicted and compared with observed values to compute prediction residuals. This procedure was repeated 20 times until all segments were left out once. The predictions residuals of each round were then combined to yield the root mean square error of cross validation process (RMSECV) and the correlation of determination when comparing both, the measured OC and predicted OC through CV (R^2_{CV}).

Throughout the cross validation process, a jack-knifing approach was adopted to determine the uncertainty estimates for the regression coefficients of the calibration models. The Jack-knifing approach estimates the variation of the CV sub-models in order to evaluate the stability of the developed model parameters. In Chapter 5, the differences between the regression coefficients (b_i) of sub-models and the regression coefficients of the total mode (b_{total}) were calculated for each compounds' OAV serving as the explanatory variable. The sum of squares of these differences led to determine the b_i variances for each predictors. These variances were then processed to establish uncertainty estimates representing 95% interval confidences on the scaled regression coefficients (Hansen et al., 2016).

An initial PLS model was initially developed with the OAV of 22 quantified odorants. Then, an iterative variable selection process was conducted by removing variables exhibiting regressions coefficients with large variance according to their Jack-knifing uncertainty estimates. Such variable removal consisted of eliminating one by one the target OAV and verifying the resulting model robustness parameters (i.e., RMSECV, R^2_{CV}) at each round.

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Chapter 3: Odor generation patterns during different operational composting stages of anaerobically digested sewage sludge

Foreword

Odors and hazardous compounds can be released all along the different operational stages of the waste treatment units. The composting process of solid wastes includes diverse odor emitting operations such as the initial waste handling, reception, storage, shredding, forced aeration treatments (active phase), turning of compostable material, curing phase and sieving of the final compost. Despite their relevance on odor regulation and management, a considerable lack of odor and chemical emissions inventories for some of these treatment stages was evidenced throughout the bibliography analysis performed in Chapter 1. In fact, except for the composting active phase, few studies have evaluated the influence of other composting operational stages on odor nuisances' generation, leading to underestimate and neglect the real environmental and health impact of the entire process.

Additionally, large amounts of anaerobically digested substrates are nowadays produced by the flourishing anaerobic industry. This new type of "solid waste" is typically post-treated through composting to warrant the stabilization of its residual organic matter, as well as remove pathogens and odorous and hazardous volatile compounds. Nevertheless, the impact of this refining process on odor and air pollution has been barely discussed in previous research works.

In this chapter, a pilot-scale experiment was carried out to evaluate the patterns of odor generation and odorants composition over different operational stages of the composting process of anaerobically digested sewage sludge (ADS). This study had two-fold objectives to tackle the lack of odor and compound emission inventories for ADS post-treatment, but also acquire general insight into the odor impact of the diverse operational stages constituting the composting process.

To achieve these objectives, gas emissions released during each composting operational stage were collected and analyzed by dynamic olfactometry and chemical methods. The odor emission rate trends (OER) through the entire process highlighted the relevance of two critical odor emission events: the early active composting phase and the turning of the compostable substrate. As a response to the substrate stabilization, OER tended to drop for the further process stages such as the later active phase and curing step. The results also showed that the odor potential trends along the process were simultaneously accompanied by a shift in the type of molecule driving the odor stimuli. Notably, different volatile sulfur compounds (VSC) governed the odor episodes depending on the composting stage. Both, odor composition and potential patterns were easily visualized in a PCA explaining 77% of variability on odor concentration (OC) and odor activity values (OAV).

Odor generation patterns during different operational composting stages of anaerobically digested sewage sludge

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Abstract

This study aimed to evaluate the global patterns of odor generation and odorant composition for different operational stages of anaerobically digested sewage sludge (ADS) composting. To this end, ADS was stored, aerobically treated, and cured in a 300 L reactor, using wood chips as a bulking agent. The compostable mixture was also turned twice. For each operational stage, odors were monitored by measuring the odor emission rates (OER in OU_E h^{-1} kg^{-1}ADS) through dynamic olfactometry and computing the odor activity values (OAV) of compounds quantified by analytical methods (i.e., GC/MS). Ammonia and volatile sulfur compounds (VSC) were the most abundant air pollutants, representing 55.5% and 20.6% of the cumulative mass emitted, respectively. The first eight days of aerobic treatment and the first turning of the compostable mixture were the critical steps for odor generation with OER ranging from 30 to 317 OU_E h^{-1} kg^{-1}ADS. Particularly, the first turning process was responsible for strong odor episodes that were emitted in a short process time (295 OU_E h^{-1} kg^{-1}ADS). Based on the OAV approach, dimethyl disulfide, dimethyl sulfide, and methanethiol were the predominant odorants along these early operational stages. Odor potential and composition shifted for the middle and later active phase, second turning, and curing stage where OER fluctuated from 0.18 to 12.6 OU_E h^{-1} kg^{-1}ADS, and hydrogen sulfide showed the most substantial odor contribution. A principal component analysis explaining 77 % of the variability in odor concentration and OAV datasets eased the recognition of these odor patterns.

Keywords: Composting stages; odor concentration; odor emission rates; odor activity values; volatile sulfur compounds; principal component analysis.

1. Introduction

Composting process is an effective and eco-friendly technology widely used to treat and valorize the increasing amount of wastes generated through anthropogenic activities (Toledo et al., 2018). The treatment of organic substrates under aerobic controlled conditions leads to obtaining stabilized and sanitized soil amendments (compost) that play a vital role in replacing fossil-fuel-based fertilizers and strengthening the entire food production chain (Wei et al., 2017). Nevertheless, composting process is also a potential source of odors and air pollutants emissions which may have a negative health impact on composting plant workers and nearby communities from composting sites (Lin et al., 2018). Nausea, hypersensitivity reactions and even alterations of the respiratory systems have been documented as common symptoms from odorants and odors exposure (Colón et al., 2017). Odors are thus the principal drawback raising public concern and complaints at neighboring areas of waste treatment units (Chen et al., 2011; Schiavon et al., 2017). The exposure risk of residents to gas emissions from composting has been aggravated due to the continuous expansion of the urban areas toward zones that were only devoted to waste treatment and disposal (Gutiérrez et al., 2017).

Solid wastes and digestates composting at large scale include diverse operational stages such as the initial waste handling (i.e., reception, storage, shredding), forced aeration treatment, turning of compostable material, curing phase and sieving of the final compost (Delgado-Rodríguez et al., 2012; Gutiérrez et al., 2015b). For solid wastes such as municipal solid wastes (MSW), sewage sludge and food waste, the active composting phase prompted by natural or forced aeration has been widely studied and reported as the main odor-causing stage (Gutiérrez et al., 2017; Toledo et al., 2018). The strong odors emitted during the aerobic treatment are principally associated with the production and release of intermediaries from anaerobic and aerobic metabolism of organic matter, but also the stripping of molecules already embedded into the organic matrices (Scaglia et al., 2011). Volatile organic compounds (VOC) and particularly volatile sulfur compounds (VSC) have been identified as the primary sources of odor pollution upon waste decomposition (He et al., 2018; Maulini-Duran et al., 2013).

In contrast to the composting active phase, few studies have evaluated the influence of other composting operational stages on odor nuisances' generation, leading to underestimate and neglect the real environmental and health impact of the entire process. For instance, the waste reception building and warehouse from waste treatment units have been reported to cause extremely offensive odors and hydrogen sulfide emissions (Delgado-Rodriguez et al., 2012; Colón et al., 2017). Fischer et al. (2008) revealed that the turning and sieving of fresh compost were the critical steps for olfactory nuisances when assesing diffused gas emission from a open pile composting facility.

Anaerobic digestion (AD) is used in 89% of EU member countries to treat and stabilize sewage sludge (Kelessidis and Stasinakis, 2012). The ultimate goal of applying AD as a waste recycling technology

is to obtain high value-added end products such as biogas and digestate (Lin et al., 2018). Notably, the anaerobically digested sewage sludge (ADS) contains high nutrient levels which may respond to the large demand of soil conditioners and fertilizers (Chen et al., 2011). However, the direct spread of ADS on crops and lands is constrained by the presence of pathogens, residual unstable organic matter, high humidity content and overall a significant risk of ammonia and odor emissions upon spreading (Wojnowska-Baryła et al., 2018; Zeng et al., 2016). Because of these shortcomings, digestates are composted prior use in agriculture (Arab and McCartney, 2017; Zeng et al., 2016). Although this aerobic post-treatment can warrant the final stabilization and lowered the odorous emission potential of ADS, this process is by itself a source of odor annoyances and air pollutants emissions.

Compared to solid waste composting, a limited number of studies have assessed odor and pollutants emissions along post-treatment of digestates. Drennan and DiStefano (2010) simulated the curing of a solid digestate derived from food and landscape wastes, providing the first hint about odors generation based on the VSC emission dynamics. For ADS composting, most of the research work has been typically focused toward the study of VOC, NH_3, and N_2O emission trends along the composting active phase (Maulini-Duran et al., 2013; Pagans et al., 2006; Zeng et al., 2014). However, there is still a gap of knowledge concerning the global patterns of odor emission and composition throughout the different operational steps of ADS composting.

Identifying the major odor-causing compounds and odor emission trends during the different operational composting stages is essential to implement proper odor mitigation strategies at waste treatment units. Odors can be monitored by sensory and instrumental-based methods. One of the most commonly employed sensory techniques is dynamic olfactometry that enables to quantify the odor concentration in European odor units (OC in OU_E m^{-3}). OC measurement consists in determining the dilution factor in which half of a calibrated odor panel perceive odor stimuli when assessing diluted gas samples (EN13725, 2003). In contrast, analytical methods such as GC/MS allows to elucidate and measure the chemical composition of the odors (Capelli et al., 2008). The chemical concentration of a substance can then be compared with its odor detection thresholds (ODT) to yield the odor activity value (OAV), a dimensionless parameters that reflects the odor nuisance potential of each volatile compound constituting the gas mixture. In theory, compounds with OAV superior to one can be linked to odor annoyances (Wu et al., 2017). The major drawback associated with OAV assessment is the significant variability of published ODT which may differ from several orders of magnitude in the literature (Parker et al., 2012).

Even if composting is profiled as a proper waste disposal technology, there is a strong need for describing the inherent negative impacts of each operational stage of this process on odor and pollutants emissions. In this study, we aimed to identify and analyze the global patterns of odor generation and odorant composition throughout the different operational steps of ADS composting. To this end, odors

were monitored through four different composting operations: storage, composting active phase (forced aeration treatment), turning process and curing phase. Odor assessment consisted of the odor emission rates (OER) measurement and OAV calculation for 84 collected gas samples. OC and OAV datasets were also explored by a principal component analysis to highlight and simplify the recognition of the most relevant patterns of odor generation.

2. Material and methods

2.1. Substrate origin and characterization

The anaerobically digested sewage sludge (ADS) was collected in a wastewater treatment plant (WWTP) located in Britanny, France. The WWTP accounts for a biological treatment unit enabling the secondary treatment of household sewage from 6611 inhabitants and wastewater from local industries. In this plant, the resulting secondary sewage sludge is valorized in situ through a wet anaerobic digestion process including two mesophilic stages at 37 °C and 20°C. The digestate is centrifuged, limed and stored before being composted or directly spread on nearby crops. Approximately 80 kg of the digestate solid fraction was collected after lime (CaOH) addition and stored in 50 L plastic bags at -20°C. Three days before running the composting experiments, frozen samples were thawed at room temperature. The physicochemical characteristics of the collected AD sewage sludge are presented in Table 1. The physicochemical characterization methods are described by De Guardia et al. (2010) and summarized in Supplementary material 1 (Section 1).

Table 1. Physicochemical characteristic of the anaerobically digested sewage sludge

Parameters[a]	**Value ± SD**[b]
Volumetric mass (kg m^{-3})	768.15
Moisture (% WB)	82.14 ± 0.021
Organic matter (% WB)	12.39 ± 0.21
Total carbon (g C kg^{-1})	64.37 ± 0.41
Total Kjeldahl nitrogen (g N Kg^{-1})	11.54 ± 0.56
Ammoniacal nitrogen (g N-NH_4^+ Kg^{-1})	1.52 ± 0.05
Chemical oxygen demand (g O_2 Kg^{-1})	131.65 ± 2.44
pH	8.15 ± 0.01

[a]Calculated on a wet mass basis (WB).
[b]SD: Standard deviation derived from 3 measurements.

2.2. Composting reactor and turning simulation device

A composting device consisting of a 300 L stainless steel pilot was used to simulate three different stages of AD sewage sludge composting: storage, active phase and curing phase (Fig. 1). The airtight composting pilot (high: 930 cm, diameter: 69 cm) was isolated by a 10 cm layer of polyurethane and contained a metallic grid (8 mm mesh) at 13 cm above the reactor's bottom to place the organic substrate. A metallic cone-shaped lid sealed the upper part of the reactor. The top covering was connected to a gutter to collect condensates, a gas exhaust outlet, and an upper air inlet. For storage and curing phase, the upper air inlet was opened to provide the reactor with surface aeration (SA). Contrarily, positive forced aeration (PFA) was set to simulate the active composting phase. To this end, the air inlet located below the metallic grid was opened to mechanically supply the reactor with an upward air inflow that crossed the organic matrix evenly. The air inflows were continuously regulated and measured through a flow meter (FL-821-V, OMEGA engineering Inc) and a volumetric gas meter (Gallus 2000, Actaris, Liberty Lake). Three Pt100 probes placed at different heights (low, middle, top compost pile height) in the compostable substrate monitored the temperature in continuous. A digital load sensor (X201-B, PRECIA MOLEN) measured the substrate weight along the composting process. Leachates were collected through an outlet placed at the pilot's bottom.

The gas exhaust was first channeled to a 5 L glass bottle to trap condensates and then transferred toward an acid traps system, gas analyzer, and gas sampling point (Fig.1). O_2, CO_2, N_2O, and CH_4 were measured in the incoming and out-going gases. A paramagnetic analyzer (MAGNOS 206, ABB) quantified the O_2, whereas an IR spectrometric analyzer (URAS 26, ABB) monitored CO_2, N_2O and CH_4 concentrations. Pressure, moisture, and temperature of the air inflow were measured constantly by a pressure (PTX510, DRUCK) and dew point/temperature (VAISALA) transmitter. The dry-air molar flow rate was expected to remain constant along the system. The molar outflow rate of water vapor was then calculated by assuming that gas exhaust was water-saturated (Blazy et al., 2014). The difference of O_2 concentration at the reactor's inlet and outlet allowed computing the oxygen uptake rate (OUR in mg O_2 h^{-1} kg^{-1} OM_0) (Adani et al., 2004; de Guardia et al., 2010).

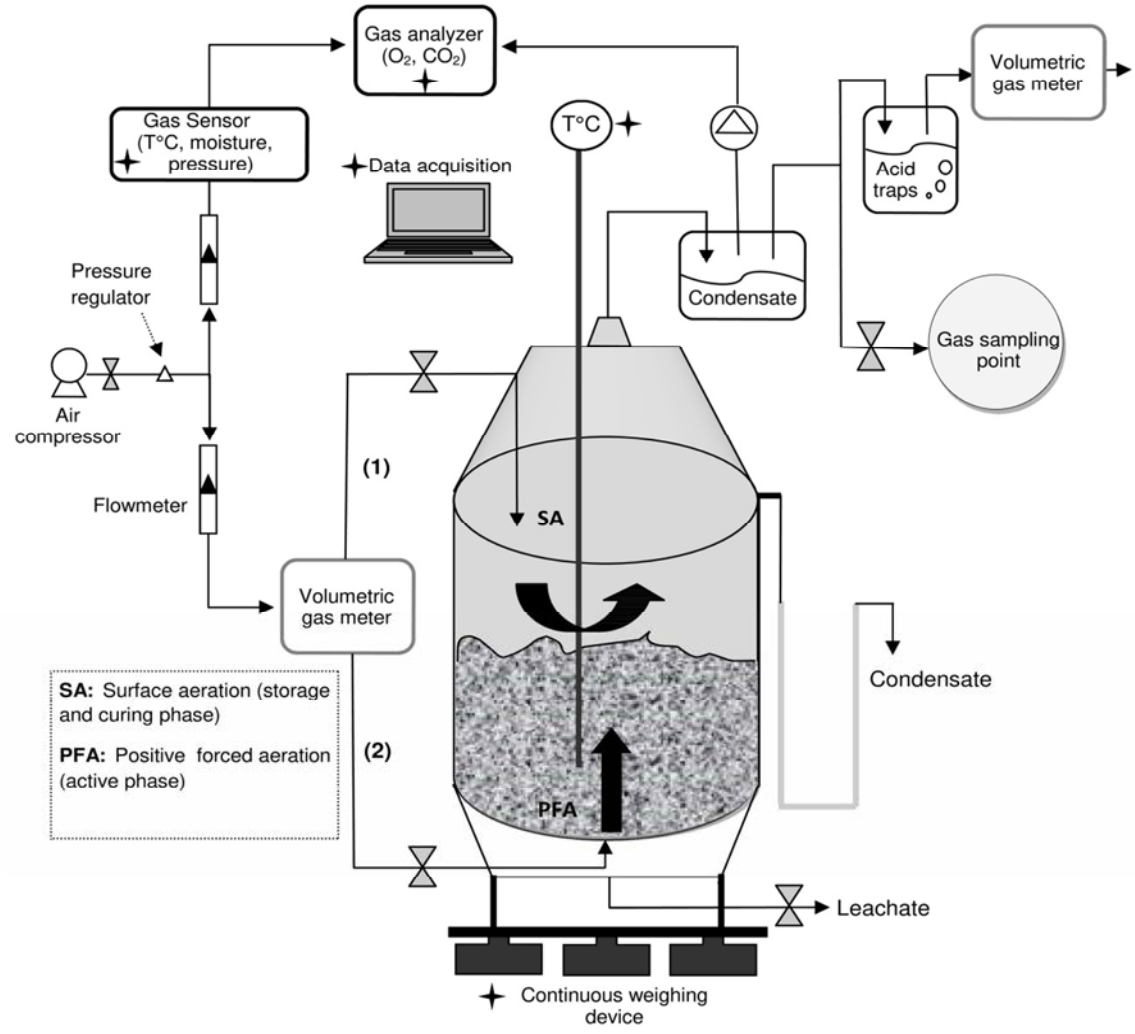


Fig. 1. Composting device and gas monitoring system. Two reactor configurations were set: **(1)** surface aeration (SA) to simulate the storage and curing phase; and **(2)** positive forced aeration (PFA) to simulate the active composting phase

The turning process of compost at pilot-scale comprised emptying the composting reactor, mixing the treated substrate manually and refilling the pilot to continue the aerobic degradation process. An experimental device was developed to sample and assess the gas emissions released during the turning process of ADS composting (Fig. 2). This device consisted of four airtight plastic containers (volume: 25 L) connected in series that were supplied with surface aeration (SA). Each plastic container was first filled with the compostable material collected along the gradual emptying process of the reactor by selecting samples located at different heights in the composting pile (bottom, middle and top). Air inflow was then set and controlled by a flow meter (FL-821-V, OMEGA engineering Inc) and a volumetric gas meter (Gallus 2000, Actaris, Liberty Lake). The resulting outflow was conveyed toward an acid traps system and a gas sampling point which were continuously monitored by a volumetric gas meter. Once surface aeration was applied, the turning process was simulated by agitating manually the compostable mixture placed inside the plastic containers one time for 30 seconds.

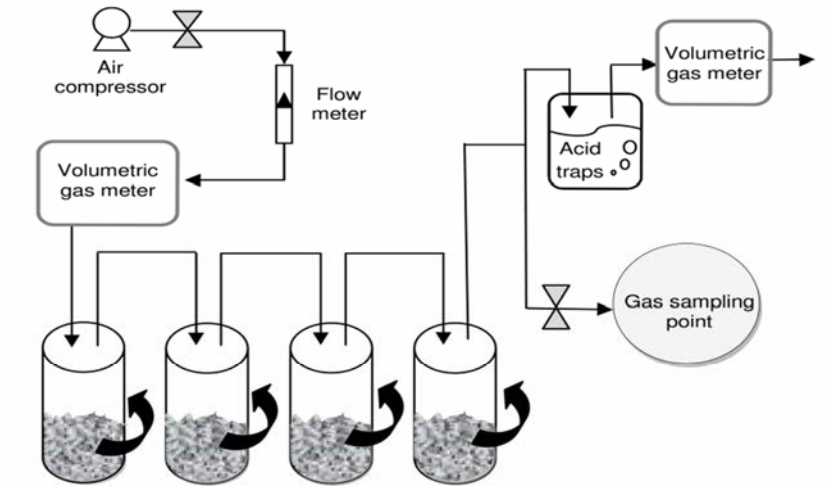


Fig. 2. Experimental device used to study the gas emission released throughout the turning process of compostable substrates

2.3. Experimental composting conditions

The composting experiment began by simulating the storage of AD sewage sludge for 8 days. The organic matrix was inserted into the described 300 L pilots (section 2.2) with a constant surface airflow of 55.8 L h^{-1} (0.149 m^3 h^{-1} m^{-2} reactor area). After this first storage stage, the reactor was emptied, and the organic matrix was mixed with wood chips (particle size <40 mm) at a volumetric mixing ratio of substrate to bulking agent (BA) of 1:1.6 (weight ratio: 0.55) to provide higher porosity and reduce substrate moisture. To prompt the active composting phase, the compostable mixture was then subjected to positive forced aeration with a constant upward air inflow of 279 L h^{-1} for 30.3 days. Throughout the active composting phase, two turnings procedures of compostable material were conducted at the 8th and 21st days of the aerobic treatment. The odor emissions produced upon turning process were assessed by introducing approximately 23 kg of the compostable mixture ready to be turned into the sampling device detailed in Fig. 2. The compostable material selected to simulate the turning process was collected at different heights of the composting pile while gradually emptying the reactor. Surface air inflows of 669 and 892 L h^{-1} were steadily applied during simulation of the first and second turning, respectively. Once finished the active phase, the resulting mixture of stabilized compost and BA was not sieved. This mixture was then cured for 26.6 days with constant surface air inflow of 56.2 L h^{-1} (0.15 m^3 h^{-1} m^{-2} reactor area). The experimental conditions used at different stages of the aerobic process are listed in Table 2.

Table 2. Experimental conditions used at different stages of the composting process

	Composting stage				
	Storage	**Active phase**	**First turning[b]**	**Second turning[b]**	**Curing phase**
Substrate mass (kg)[a]	71.4	70.9			
Bulking agent mass (kg)[a]	0	38.9			
Ratio BA/S (kg kg^{-1})[a]	0	0.55			
Mixture mass (kg)[a]		109.8	22.9	22.6	81.3
Initial moisture (%)[a]	82.1	57.9			
Mean aeration rate (L h^{-1})	55.8	279	669	892	56.2
Stage duration (days)	7.8	30.3	0.08	0.14	26.6
Type of aeration[c]	SA	PFA	SA	SA	SA
Gas samples	12	30	9	9	24

[a]Wet mass basis
[b]The compostable mixture was turned at the 8th and 21 days of aerobic treatment.
[c]Surface aeration (SA) and positive forced aeration (PFA).

2.4. Gas sampling and analytical methods

Exhaust gases coming out from the reactor first crossed a 5 L glass bottle at room temperature to condense any water excess that could interfere upon analytical and sensory measurements, especially throughout the active composting phase. A total of 84 gas samples were collected during the different stages of composting (Table 1). Notably, only three gas samples were taken during 2.5-3 hours during turning simulation. Gas sampling was performed by filling 30 L single-use nalophan bags according to the EN 13725 recommendations (EN 13725, 2003). For the composting reactor and turning device, the channeled exhaust air stream enabled to fill the gas bags automatically in approximately 15 or 30 minutes depending on the applied air inflow. Gas samples were shortly analyzed within a time frame of 3-6 hours to prevent chemical compound losses and collateral chemical reactions among volatile compounds. According to Mochalski et al. (2009) and Van Harreveld (2003), odor and chemical measurements conducted using nalophan bags are more reliable if storage time is limited to six hours.

Ammonia emitted along each composting phase was absorbed by an acid trap system consisting of two glass impingers filled with 200 mL of sulfuric acid (H_2SO_4 4%). Acid traps were analyzed through the modified method NF T 90-015-1 and changed before gas sampling was carried out. Trapped ammonia was then released by steam distillation in the presence of sodium hydroxide (NaOH, 32%), recovered into a boric acid solution (H_3BO_3, 40 g L^{-1}) and quantified by back-titration with H_2SO_4 (0.2 N) in an automated titration unit (Gerhardt Vapodest 50s). The method detection limit was 0.29 mg m^{-3}.

Volatile organic compounds (VOC) were quantified by a GC/MS (Clarus 500 GC-MS, Perkin Elmer, USA) coupled to a thermal desorption unit (TurboMatrix 550, Perkin Elmer). VOC contained in the nalophan bags were concentrated and adsorbed onto carbotraps (349, Perkin Elmer) at a flow rate of 51.8

mL min^{-1} by a calibrated vacuum pump (Gilair3). VOC were desorbed by the thermal desorption unit (200°C) and separated in a capillary column CP-WAX 58 (25m x 0.15 mm x 0.25μm, Varian, USA) using helium as a carrier gas (1 mL min^{-1}) and a pressure column of 310 kPa. The GC oven temperature was first held at 40°C for 5 min, then ramped to 180°C at 10°C min^{-1} and finally kept at 180°C for 5 min. VOC were identified by verifying their retention times with standards and performing a spectral mass comparison (from 20 to 300 atomic mass units-uma) with a reference library (NIST 2012, National Institute of Standards and Technology). A full scan and single ion monitoring (SIM) mode were employed to acquire and integrate the identified diagnostic ions (m/z). VOC quantification was conducted through external calibration ($R^2 > 0.95$) with chemical standards (Purity > 98%, suppliers: Fluka, Fisher, Janssen Chemical, Sigma Aldrich, Across Organic and Alfa Aesar). The relative chemical concentrations of formamide, 2-nonanone, thujone, and thymol were computed through the obtained mean calibration coefficient (630) from available standards. MDL were yielded by interpolating the minimum amount of standard to obtain a ratio signal to noise equal to 3 (Defoer et al., 2002). The MDL varied from 0.008 to 3.7 ng (Table 3). Similarly, the mean recovery rates of VOC when using nalophan bags at a storage time ranging from 3-6 hours are provided in Table 3.

Volatile sulfur compounds (VSC) were analyzed by a micro GC coupled to an electrochemical detector (airMEDOR, Chromatotec) according to the norm ISO 6326-2 (1981). Hydrogen sulfide (H_2S), methanethiol (CH_3SH), ethanethiol (CH_3CH_2SH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) were analyzed by injecting the sampled gas exhaust collected in nalophan bags into a 400 μL loop valve at a flow rate of 100 mL min^{-1} to be then separated through a capillary column (1.2 m x 1.6 mm x 180 μm) and an airflow of 4 mL min^{-1}. Column temperature and pressure were set to 40°C and 230 hPa during the analysis. Resolved VSC consequently underwent redox reactions in an electrochemical detector containing chromic oxide solution (CrO_3, ten %w). The resulting electric potential differences were measured and recorded in continuous. Sulfur compounds were quantified by external calibration ($R^2 > 0.94$) with standard compounds (>98.5 %; Sigma-Aldrich and Across Organics) and reference gases (200 ppm standards of H_2S and CH_3SH; Air Liquid). The MDL were calculated by taking into account 1000 unit area as the minimum area possibly detected by MEDOR. MDL ranged from 0.008 to 0.015 ng. VSC recoveries for a storage time from 3-6 hours in nalophan bags are presented in Table 3.

The chemical concentrations of ammonia, VSC and VOC are presented in Supplementary material 2. The cumulative mass production (μg Compound kg-1) of these pollutants at each composting stage was calculated and expressed as a ratio of the initial wet weight of AD sewage sludge (kg) for a given constant airflow. This term relating the total amount of emitted compound to the amount of treated organic substrate is also called emission factor (Maulini-Duran et al., 2013).

2.5. Odor activity values (OAV)

The odor activity value of each quantified volatile compound (OAV_i, dimensionless) was determined (Supplementary material 3) as the ratio of the substance's chemical concentration (C_i in mg m^{-3}) to its odor detection threshold (ODT_i in mg m^{-3}) as shown in Eq. (1).

$$OAV_i = \frac{C_i}{ODT_i} \quad \text{Eq. (1)}$$

Nine ODT previously measured by dynamic olfactometry (Rincon et al., 2019) were employed to calculate OAV (Table 3). Notably, the calibrated panel assessing the composting gas exhaust was the same who conducted the ODT measurements. The ODT of ten analytes were not measured. In this case, ODT from Nagata (2003) report were considered to compute OAV. Consequently, the cumulative OAV of each substance ($\sum OAV_i$) at each process stage was compared to the sum of the cumulative OAV from all detected odorants in the gas mixture ($\sum OAV_{sum}$) to yield the percentage of odor contribution (PO_i, Wu et al. 2017), as shown in Eq. (2).

$$PO_i = \frac{\sum OAV_i}{\sum OAV_{sum}} * 100\ \% \quad \text{Eq. (2)}$$

2.6. Sensory measurements

A minimum of 5 selected and screened human subjects assessed the odor concentration (OC) in European odor units (OU_E m^{-3}) of composting gas exhausts through dynamic olfactometry (EN 13725, 2003). Generally, two or three replicates were presented to a trained panel using a dynamic olfactometer ONOSE 8 (Consumaj) equipped with calibrated air mass flow controllers. If required, gas samples were pre-diluted 100 folds with a tight gas syringe before evaluating OC (Blazy et al., 2015). The raw or pre-diluted gas samples were diluted with neutral gas (analytical grade air) and presented in an ascending concentration order to determine the dilution factor at the 50% detection threshold (Z_{50}). Dilutions were performed at a step factor of 2 with an available dilution range varying from $2^{2.7}$ to $2^{15.7}$. According to EN 13725, Z_{50} is equal to OC at the standard conditions for olfactometry. Dilutions were presented in a forced choice mode involving the detection of an odor stimulus from odorless gas in a three-port sniffing station. The average ODT resulting from n-butanol calibration (Sigma-Aldrich, 99.9%) of 11 panelists was 120 ± 56 μg m^{-3}, thus complying with the EN 13725 quality requirements (62-246 μg m^{-3}).

The odor emission rates (OER in OU_E h^{-1}) were calculated as a product of the OC geometric mean from the tested replicates (OU_E m^{-3}) and the mean airflow rates (m^3 h^{-1}) at each composting stage. OER was reported as a ratio of initial organic matter content (OU_E h^{-1} kg^{-1} OM_0). Moreover, the odor emission factor (OEF) was obtained by the integration of OER throughout the respective composting stage

duration. OEF is a term analogous to the emission factor that links the overall quantity of odor produced to specific parameters intrinsically involved in odor generation (Rincón et al., 2019). For waste treatment units, this specific activity index can be the plant weight capacity or surface area (Lucernoni et al., 2016). In the case of this pilot study, OEF were related to the initial wet weight of ADS to be composted (OU_E kg^{-1}).

2.7. Data analysis

A principal component analysis (PCA) was conducted by The Unscrambler X version 10.5 (CAMO) on the output datasets from OAV calculation and OC measurement (Supplementary material 3) to visualize the odorant composition and potential at the different stages of ADS composting. PCA is a multivariate analysis method based on the linear dimensional reduction of data to easily recognize patterns among the tested samples and variables (Gutiérrez et al., 2015a; Toledo et al., 2018). Before conducting the multivariate analysis, OC and OAV were logarithmically transformed to reach normal data distribution. This scaling process limited background noises caused by irrelevant variation and highlighted correlation patterns among variables. Furthermore, the dataset's missing values caused by non-detected compounds were substituted by half of their detection limits to perform the statistical treatments of data (Blanes-Vidal et al., 2009; Susaya et al., 2011). The outcomes from the PCA were plotted in the scores plot and correlation loadings plot. The scores plot led to identifying samples patterns and clusters, whereas the correlation loadings plot allowed estimating how much each variable contributed to explain the data variance on the PCA model components (Toledo et al., 2018). One outlier was detected for the first turning process and, it was discarded before constructing the PCA model.

3. Results and discussion

3.1. Composting performance

The trend profiles of oxygen uptake rate (OUR) and temperature were studied to provide insight into the substrate stabilization evolution at each composting stage (Fig. 3). Despite being supplied with enough oxygen (2 gO_2 h^{-1} $kg^{-1}OM_0$), ADS storage was characterized by low OUR inferior to 145 mgO_2 h^{-1} $kg^{-1}OM_0$. During this stage, semi-anaerobic conditions were settled as a result of the low gas transfer toward the inner sections of the stored pile (Arab and McCartney, 2017; Schlegelmilch et al., 2005). Likely, the high humidity and bulk density of ADS (Table 1) played a vital role in limiting the free air space in the pile and the low aerobic microbial activity. The formation of reducing conditions and anaerobic zones inside the stored digestate favored the occurrence of potential odorants as discussed in section 3.2.

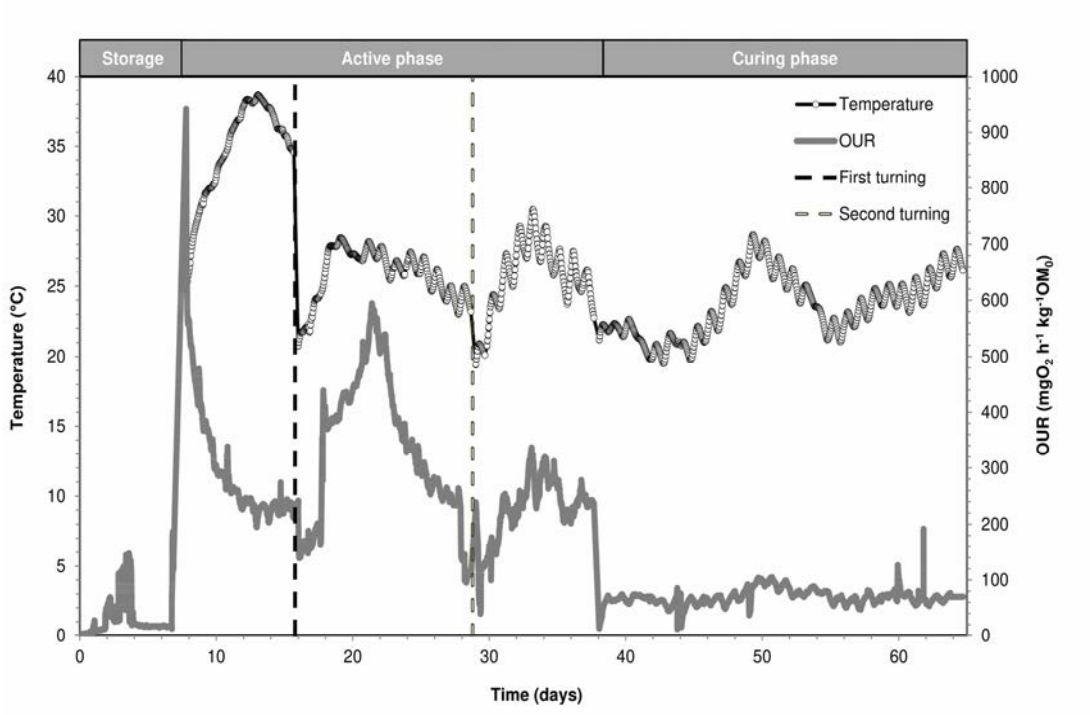


Fig. 3. Oxygen uptake rates (OUR) and temperature throughout the operational composting stages of anaerobically digested sewage sludge (ADS)

Once aerobic conditions were prompted through bulking agent addition and PFA application, the OUR kinetic (Fig. 3) showed a sharpened peak at 7.8 days, reaching a maximal oxygen consumption of 940 mgO_2 h^{-1} $kg^{-1}OM_0$. Likewise, the maximum temperature (38°C) along the process was evidenced after two days of setting the forced aeration. The first ten days of aerobic treatment accounted for around 28 % of the net cumulative oxygen consumption. Zeng et al. (2014) reported a similar O_2 consumption trend upon ADS aerobic treatment, documenting a maximum OUR of 1333 mgO_2 h^{-1} $kg^{-1}OM_0$. The oxygen supplied (9.6 gO_2 h^{-1} $kg^{-1}OM_0$) throughout the active phase was ten times superior to the maximal OUR.

Such aeration surplus had not only adverse effects on energy costs but also produced a cooling effect of the composting pile that might have hindered the thermophilic phase attainment (T> 45°C) (Zeng et al., 2016).

After rapidly decomposing the readily biodegradable organic matter in ADS during the first day of forced aeration, microorganism tended to consume less oxygen and OUR dropped right after the second turning (Fig. 3). OUR peaked at 21.4 days (594 mg O_2 h^{-1} kg^{-1} OM_0) because the turning process improved the substrate porosity and made oxygen accessible for zones not supplied with O_2. Previous studies have proposed an OUR value of 500 mgO_2 h^{-1} $kg^{-1}OM_0$ as an indicator of biological stability during the composting process (de Guardia et al., 2010; Drennan and DiStefano, 2010). By considering this stabilization criterion, ADS was expected to be fully stabilized after 22.5 days of composting. However, the low measured OUR and cumulative oxygen consumption (231 gO_2 Kg^{-1}ADS) through the biological process indicated a high degree of organic matter stabilization for ADS. During anaerobic digestion, most of the readily biodegradable organic matter (i.e., proteins, sugar) is decomposed. As a result, digestates contain principally complex molecules such as polysaccharides and lignin that are not easily accessible to the microorganisms (Provenzano et al., 2014).

3.2. Emission factors at different stages of ADS composting

3.2.1. Emission factors of air pollutants

A total of 19 compounds were identified and quantified throughout the different stages of ADS composting. The emission factors of the detected pollutants, the key parameters involved in their quantification, and their odor detection thresholds are listed in Table 3. Notably, the resolved substances were grouped into six chemical families including N-containing compounds, volatile sulfur compounds (VSC), ketones, alcohols, terpenes, and volatile organic acids. In general, the total mass emitted along the entire process was attributed to ammonia (55.5%), acetic acid (17%), DMDS (8.9%), H_2S (6.4%), DMS (4.7%), methanol (2.3%), limonene (1%), ethanol (1%), α-pinene (0.8%), and methanethiol (0.6%). The emission profiles for these substances are provided in Supplementary material 1 (Section 2). VSC were the most emitted compounds after ammonia with an overall mass contribution of 20.6%. In line with our results, sulfur compounds have been formerly targeted as leading pollutants and predominant odorants upon management (i.e., drying, centrifugation and storage) of biosolids cakes in WWTP (Chen et al., 2011; Novak et al., 2006).

Table 3. Odor and emission factors obtained along the different operational stages of ADS composting

							Emission factors (μg kg^{-1})[a]				
Family	Compound	m/z[b]	MDL[c] (ng)	Calibration Coefficient[d]	Recovery rates (%)[e]	ODT (μg m^{-3}) [g]	Storage	Active phase	First turning	Second turning	Curing phase
N-containing compounds	Ammonia	-	-	-	89±6[f]	***1810***	3384	15484	264	18.5	223
	Formamide	45	-	630	-	147400	1.25	106	2.60	1.39	0.83
Volatile sulfur compounds	Hydrogen sulfide	-	0.011	34817	105±4	***0.47***		2112	1.71	44.2	68.5
	Methanethiol	-	0.008	48205	104±1	***0.21***	22.9	181	1.19		
	Dimethyl sulfide	-	0.015	26018	104±1	***6.9***		1644	13.2		
	Dimethyl disulfide	-	0.013	29497	110±1	***9.8***	1875	1223	5.83		
Ketones	Acetone	58	0.07	318	77±17	101000	28.0	46.7	0.79	8.78	0.52
	2-butanone	72	0.016	407	82±13	1300	10.39	2.25	0.02	5.75	0.16
	2-nonanone	58	-	630	-	32	1.73	14.2	0.08		0.01
Alcohols	Methanol	31	0.139	571	106±15	43000		604	6.09	193	3.71
	Ethanol	31	0.097	800	100±13	990	5.19	244	4.33	91.5	1.22
Terpenes	α-pinene	93	3.77	123	76±26	***220***	89.1	174	3.42	15.2	4.92
	3-carene	93	0.6	365	-	9300	28.8	74.2	0.32	0.02	1.57
	Limonene	68	0.69	206	105±0.1	***180***	83.3	262	3.98	0.64	9.37
	p-cymene	119	0.23	841	-	***120***	40.6	104	0.54	10.6	2.71
	Thujone-1[h]	110	-	630	-	24000	7.50	47.2	0.50	0.23	2.60
	Thujone-2[h]	110	-	630	-	24000	1.84	35.7	0.38	0.09	0.68
	Thymol	135	-	630	-	50	3.00	15.7	0.07	0.02	1.29
Acid	Acetic acid	60	0.79	61	70±10	***19***	60.9	4702	39.3	1099	43.1
Total emission (μg kg^{-1})[a]							5643	27074	348	1489	364
Odor emission factor (OU_E Kg^{-1})[a]							611	10772	590	21	149

[a]Expressed as a ratio of the initial wet weight of AD sewage sludge. [b]Mass to charge ratio. [c]MDL: method detection limits; - :not determined. The MDL for NH_3 was 0.29 mg m^{-3}.
[d]Calibration coefficient. Compounds with a calibration coefficient of 630 were semi-quantified.
[e]Mean recovery rates after 3-6 h of storage in nalophan bags. [f]Recovery rate documented by Sironi et al.(2014).
[g]ODT: Odor detection threshold in bold italics were measured by dynamic olfactometry (Rincón et al., 2019). Underlined ODT were obtained from Nagata (2003).
[h]Thujone's isomers were not resolved.

The different operational stages of ADS aerobic post-treatment contributed differently to the total emission of contaminants. For instance, the storage and active composting phase of ADS were the primary sources for air pollution by releasing 16% and 77% of the overall mass of compounds, whereas the curing and turning process only accounted from 1% to 4%. The emitting potential of ADS was reduced in 89.8% after being subjected to the aerobic treatment. Indeed, most of the VSC were eliminated or drastically reduced by the end of the curing process (Table 3). H_2S was the only VSC produced throughout curing, exhibiting concentrations inferior to 0.16 ppm. Nevertheless, H_2S was also abated in a 97% when compared to its cumulative mass during the active phase. Drennan and DiStefano (2010) proved that curing digestates for 15 to 20 days can diminish the emission of VSC to concentration levels varying from 1 to 5 ppm. According to our results, a better VSC removal can be achieved by applying an aerobic treatment before carrying out the curing step.

The first eight days of the active composting phase herein called "the earlier active phase" were responsible for 40% of the total mass of volatile compounds released during the entire composting simulation. This marked increase in pollutants emissions along the first days of the aerobic treatment was consistent with the rise in temperature and OUR previously discussed in section 3.1. As expected, PFA led to greater emission rates of air pollutants and odorants because of the stripping and volatilization of compounds embedded into the organic matrix or produced as intermediaries of the substrate decomposition (Staley et al., 2006). Likewise, the rise in temperature resulting from organic matter mineralization may have triggered the release of volatile compounds along the aerobic treatment. Finally, the rapid oxygen consumption by the microorganisms to degrade the readily organic matter at the first day of aerobic treatment (Fig. 3) has been linked to the formation of anaerobic zones into the biofilms-particles and higher VOC production (Maulini-Duran et al., 2013; Scaglia et al., 2011).

3.2.2. Speciation of volatile compounds

The chemical emission patterns for the most abundant compounds released during ADS composting were displayed in Fig. 4. Since the nature and abundance of the occurring substances significantly differed from the start to the end of the active phase, this stage was divided into the earlier (first eight days of the aerobic treatment), middle (8-21 days of the aerobic treatment), and later active phase (21-29 days of the aerobic treatment). The resulting active phase sections matched with the performed turning process. For instance, the middle active phase was placed between the first and second turning process.

Ammonia was the leading volatile compound constituting the gas exhaust along the different stages, which may be associated with the ongoing ammonification and stripping process along composting (Zeng et al., 2012), but also with the high free ammoniacal nitrogen content of ADS (ratio C/N~6). During anaerobic digestion, most of the organic N in sewage sludge is turned into its ammonical form (Zeng et

al., 2016). Free NH_3 was then actively volatilized and stripped under storage conditions and through the application of PFA as explained in Supplementary material 1 (Section 3, Fig. 2S).

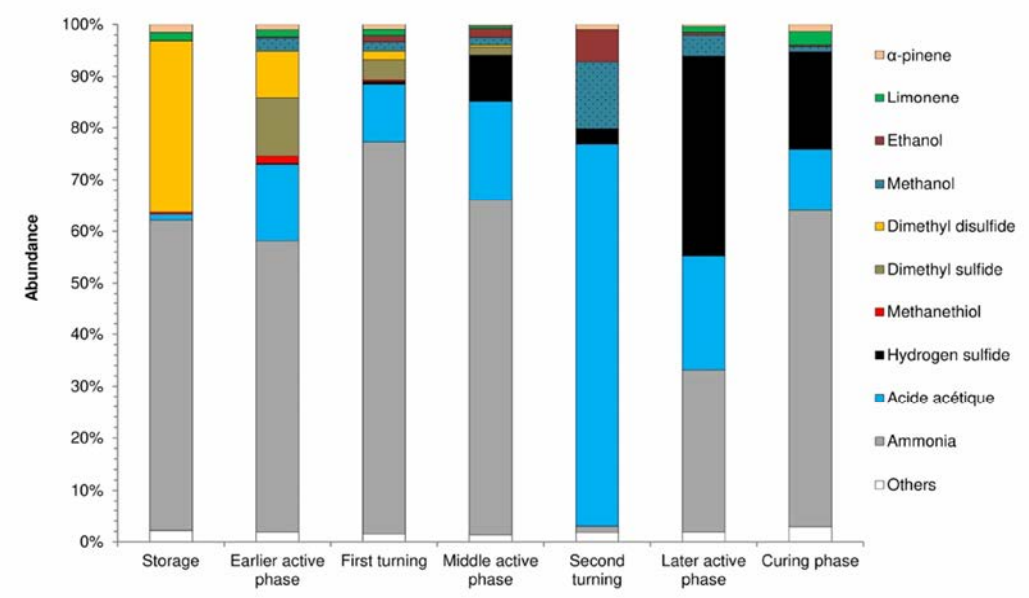


Fig. 4. Abundance (%) of the major volatile compounds emitted throughout the composting process of anaerobically digested sewage sludge. The emissions' chemical fingerprints at each composting stage are depicted

Semi-anaerobic conditions set on the composting pile had a considerable influence on volatile compounds production all along the composting process of ADS. Common intermediaries of anaerobic metabolism such as VSC and acetic acid showed abundance percentages ranging from 3% up to 38.6%, and 1% up to 74%, respectively (Fig. 4). The occurrence of these pollutants indicated that reducing conditions were present inside the composting pile even throughout the aerobic treatment. Besides oxygen depletion to mineralize the readily available organic matter, other mechanisms could have equally limited the oxygen supply in specific zones of the composting pile, namely, the establishment of preferential airflow pathways (channeling), the formation of substrate clumps, and the reduction of particle void due to material compaction over the decomposition process.

Under reducing conditions, proteins constituted by sulfur-containing amino acids (methionine and cysteine) are anaerobically metabolized, resulting in the generation and release of potential odorants such as VSC (Higgins et al., 2006). For ADS composting, DMDS was the most emitted VSC accounting for a net mass of 3.1 mg kg^{-1}ADS. DMDS exhibited a total abundance of 33% during storage where the lack of oxygen diffusion inside the composting pile prompted semi-anaerobic conditions (Fig. 4). DMDS generation is typically related to the abiotic oxidation and methylation of methanethiol (He et al., 2018; Higgins et al., 2006). Hence, the surface aeration applied upon storage could have triggered these abiotic reactions on the CH_3SH produced or already contained in the stored ADS.

The emission pattern of VSC shifted during the earlier active phase and the first turning where DMS, DMDS, and CH_3SH were simultaneously generated and released, representing from 5.8% to 21.7% of the total mass emitted (Fig. 4). These organic sulfur compounds coexisted during these early stages of the process as they are precursors for each other (Novak et al., 2006) under the possible onset of anaerobic and anoxic conditions prompted in the biofilm-particles. Once the aerobic process continued, the organic VSC were likely degraded by methanogenic and anaerobic microbial communities, leading to the production of H_2S for the middle and later active phase (9-39%), second turning (3%) and curing period (18.8%) (Fig. 4). It is known that H_2S is the final intermediary of the sulfur cycle before complete removal of sulfur gases in biosolid digestates (Higgins et al., 2006; Novak et al., 2006).

Limonene and α-pinene occurred in a minor extent during ADS composting with abundance percentages that fluctuated from 1% to 3% (Fig. 4). After the addition of wood chips to conduct the active phase, the net mass emitted of both terpenes increased from 0.17 to 0.36 g Kg^{-1} ADS. Such growing trend may be associated with the aerobic metabolism of organic matter derived from the vegetable feedstock constituting the added bulking agent (Pagans et al., 2006; Schiavon et al., 2017). Both terpenes were also generated under the oxygen-limiting conditions commonly set when storing ADS without bulking agent addition, probably because of the presence of any green and food waste (i.e., tree branches or fruit peelings) in the initially treated sewage sludge. Methanol, ethanol and acetic acid were the most abundant oxygenated molecules detected in the gas exhaust (Fig. 4). These intermediaries of anaerobic metabolism or incomplete aerobic fermentation process (Gallego et al., 2012; He et al., 2018) were considerably present while performing the second turning. This result confirmed the presence of anaerobic zones at the end of the active phase, probably due to compaction and agglomeration of the compostable substrate.

3.3. Odor emission rates (OER) and odor emission factors (OEF)

OER that integrates reactors' airflows was selected as a descriptor for odor nuisance among the different process steps. The quantified OER at each stage of ADS composting is depicted in Fig. 5. OER increased steadily during ADS storage by a factor of 10, reaching an OER of 17.6 $OU_E\ h^{-1}\ kg^{-1}$ADS on the fourth day of storage. Although ADS was highly stabilized, this substrate exhibited a strong odor nuisance potential along storage. This first result justified and reinforced the idea of applying a biological post-treatment that could avoid issues concerning odor plumes upon direct digestate spreading on crops.

The rise on biological activity and temperature (Section 3.1) during the early active phase was accompanied by a first OER peak of 56.6 $OU_E\ h^{-1}\ kg^{-1}$ADS (Fig. 5). This result suggests that high microbial activity and temperature during the early days of ADS aerobic treatment can be related to strong odor emissions episodes. Presumably, volatile compounds generated through the anaerobic and aerobic decomposition process and the stripping of already established molecules were the primary sources of

odor pollution during this phase. In accordance to our results, Gutiérrez et al. (2017) and Toledo et al. (2018) have also demonstrated that the first days of active composting phase (hydrolytic stage) of solid wastes are deeply involved in the generation of odor annoyance.

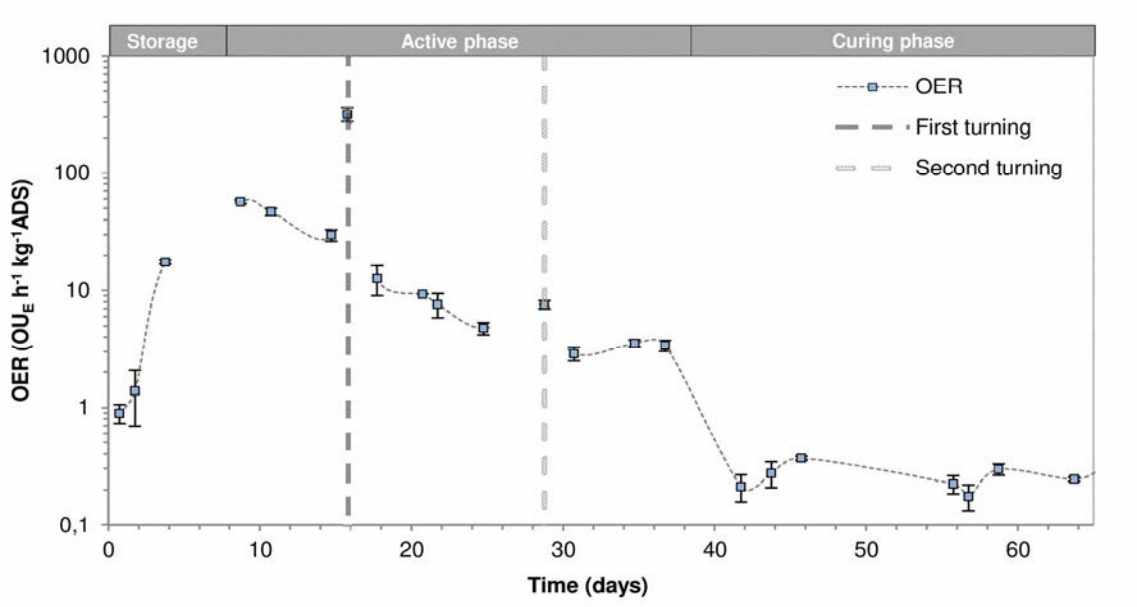


Fig. 5. Odor emission rates at different operational stages of ADS composting

A second intense OER peak (Fig 5) was detected when conducting the first turning of the compostable mixture during 2 hours. Throughout this sampling time, OER remained almost constant with an average value of 317 ± 44 OU_E h^{-1} kg^{-1}ADS. This OER value was five times higher than the one obtained at the beginning of the active composting phase, thus proving the critical influence of this operational stage on odor production along ADS composting. During the turning process, the compostable material is loosened and the solid media, including biofilm particles, are more exposed to the gas phase (El Kader et al., 2007). This increase in the contact area of the solid-gas interphase could have led to higher emission rates of volatile compounds and odors. Additionally, the high surface airflow applied (669 L h^{-1}) to simulate the turning process may have played an essential role in the OER increase.

Hanajima et al. (2010) evaluated the gas and odor emissions along swine feces composting and concluded that compost turning is a critical event for odor nuisance generation. However, only limited literature has been addressed toward the evaluation of odor exposure risk during the mixing process of compostable substrates by itself. Fischer et al. (2008) observed that diffused gas emissions resulting from the turning process of open pile compost had significant OC superior to 3000 OU_E m^{-3}. According to our results, even stabilized substrates such as digestates should be composted and turned under confinement conditions and using proper odor abatement technologies. These provisory measurements are necessary to lower the odor and chemical exposure risk of plant workers and neighbors from methanization plants accounting for aerobic post-treatment.

The second turning, which was performed at the end of the active phase (21 days of forced aerobic treatment), accounted for OER values that were 42 times lower to the ones obtained for the first mixing of compostable material. Therefore, the odor risk upon ADS turning was attenuated as the composting process proceeded. Such downward trend could be principally associated with the reduced odorants emission rates at the further stages of the composting process. By that time, most of the organic matter and volatile compounds were already degraded, stripped or volatilized. The diminution on microbiological activity and substrate stabilization was generally reflected in a decline of OER (Fig. 5). For instance, the middle and later active phase, second turning and curing process presented OER values that ranged from 0.18 to 12.6 OU_E h^{-1} kg^{-1}ADS.

The odor nuisance potential at each composting step was easily rated through their odor emission factors (OEF). According to the overall OEF (Table 3), the crucial composting steps involved in odor generation were the active composting phase (82%), storage (5%), and first turning (5%). Notably, the high impact of mixing compostable materials on odors generation was highlighted when considering the duration time for each operational stage (Fig. 6). The first turning process of compostable material accounted for an OEF per stage duration of 295 OU_E h^{-1} kg^{-1}ADS which was seven times higher than the OEF obtained during the earlier active phase (40.5 OU_E h^{-1} kg^{-1}ADS). This finding corroborated that the turning process can be the cause of strong odor episodes even if this step is conducted in a short process time (2 hours). This upward odor trend was specifically observed when turning compostable material that was not fully stabilized such the case of ADS at the 8th day of aerobic treatment.

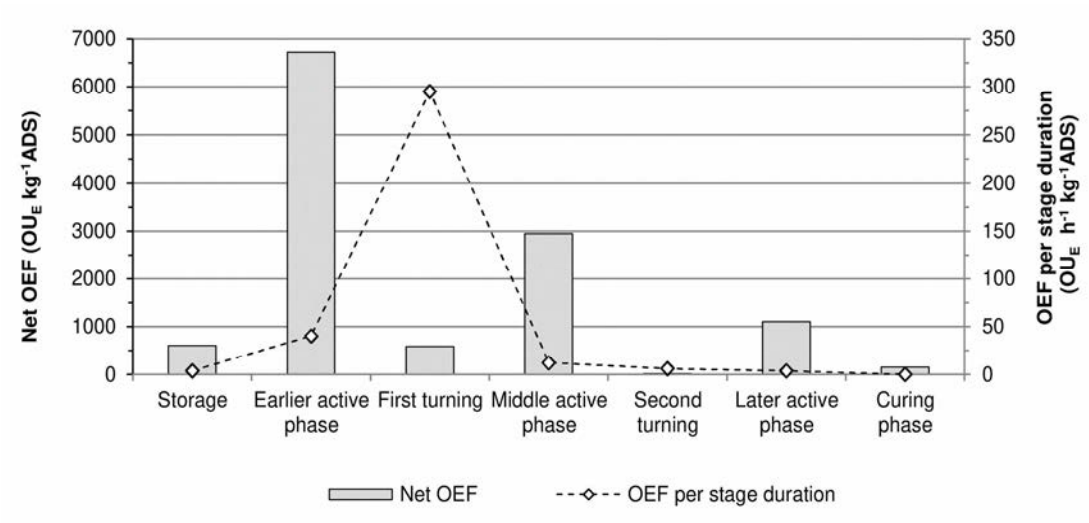


Fig. 6. Odor emission factors (OEF) for each composting stage. OEF was also expressed as a ratio of the stage time duration (hours)

Sironi et al. (2006) compared OEF values at different locations of a mechanical-biological plant treating municipal solid waste (MSW) and concluded that the active composting phase was the primary source for odor annoyances. The OEF computed from MSW aerobic treatment (140 OU_E t^{-1}) was 13

times superior to the value obtained for ADS composting, thus proving the suitability of the anaerobic digestion in alleviating the odor potential of raw substrates. OEF and OER are valuable terms to determine the odorous potential of each composting stage. Nevertheless, these parameters cannot elucidate and target the chemical compounds causing the odor troubles which are also responsible for certain odor quality features. Hence, an OAV approach was employed to attempt identifying the main substance triggering the odor episodes at each stage of ADS composting.

3.4. Odorant composition at different stages of ADS composting

3.4.1. Principal component analysis (PCA) on OAV and OC

OAV and OC datasets were explored through a PCA to recognize the most significant odor composition patterns at each composting stage (Fig. 7). The two first principal components (PC-1 and PC-2) explained 77 % of the variability in the data. The remaining PCs were not considered as they shortly upgraded the variance explanation (i.e., only 10 % when including PC-3 and PC-4) and made the model interpretation more complex. The gas samples were clustered on the score plot over the four quadrants according to the composting stage in which they were collected (Fig. 7A). In particular, samples were placed almost chronologically along PC-1 following the composting process evolution. For instance, samples obtained during the first 15 days of composting simulation and derived from the main odorous process steps according to OER (storage, early active phase and first turning; section 3.3) were located at the plot right side (positive PC-1 axis). In contrast, samples analyzed after 15 days of the process were predominantly present at the left side of the plot score (negative PC-1 axis).

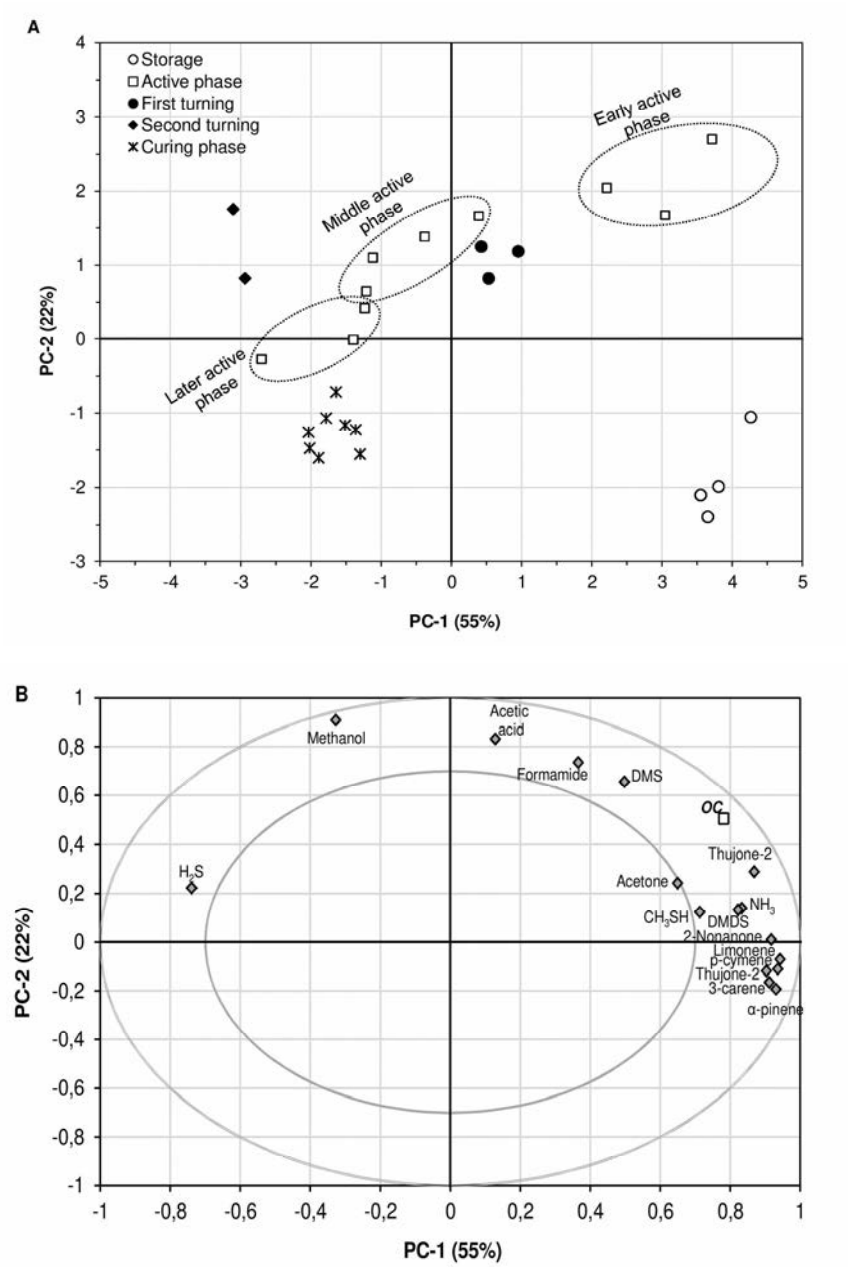


Fig. 7. Score plot (**A**) and correlation loading plot (**B**) obtained by the principal component analysis (PCA) on odor concentration (OC in OU_E m^{-3}) and odor activity values (OAV, dimensionless) of pollutants released along different composting stages (storage, active phase, first turning, second turning and curing phase) of anaerobically digested sewage sludge

Fig. 7B depicts the correlation loading plot resulting from PCA on OC and pollutants OAV. Most of the measured variables fell inside the inner and outer ellipses in the correlation loading plot, thus implying that PC-1 and PC-2 could successfully describe from 50 up to 100 % of their variability. Based on the variables closeness in the plot's upper right quadrant, OC was positively correlated with DMDS, thujone, methanethiol, acetone, NH_3, and DMS. Among these molecules, VSC were the substances exhibiting the lowest ODT (Table 3) and then high odorous potential. Even if ammonia, thujone, and acetone were not

expected to exert a substantial impact on odor perception, they showed a strong correlation with OC probably because they were simultaneously released with the critical odorants during the first days of stripping and organic matter mineralization. Similarly, Hansen et al. (2016) found a no-causal strong relationship between OC and acetone, presumably due to the coupled production of odorants and this microbial degradation intermediary.

Hydrogen sulfide and OC were located in opposite quadrants of the loading plot (Fig. 7B), indicating a negative correlation between these two variables. In other words, H_2S showed a considerable odorous potential for samples displaying reduced OC. Such a trend was further examined while comparing the score plot and correlation loading plot (Fig. 7). Odors samples collected during the first 15 days (plot's right side) of the composting process, which accounted for high OC (1130-22400 $OU_E\ m^{-3}$), were linked to the presence of DMDS, methanethiol, DMS and the rest of volatile compounds. In contrast, the odorous gas emissions (191-3120 $OU_E\ m^{-3}$) sampled along the later and middle active composting phase, second turning, and curing phase (plot's left side) were principally associated with the occurrence of H_2S.

The relevance of DMDS on odor generation throughout the aerobic treatment of ADS was similarly demonstrated by Maulini-Duran et al. (2013) in a lab-scale experiment. Novack et al. (2006) reported that volatile organic sulfur compounds typically peak at the earliest stage of ADS incubation at 20°C (1-7 days), while H_2S tended to appear at the farthest stages as a final intermediary of the sulfur cycle. According to the PCA results, this shift on the type of VSC emitted can highly impact the patterns of odor generation and perception along the different stages of ADS composting. Identifying the critical components of odors and their behavior at each step of the composting process is decisive to implement appropriate odor abatement strategies. He et al. (2018) and Blazy et al. (2014) determined that changing some operational composting parameters (i.e., amount of bulking agent and aeration rate applied) can be a cost-effective way to reduce VSC emissions. Enclosing gas exhausts (confinement) and treating them by end-of-pipe technologies such as biofilters, regenerative gas scrubbing, and adding reagents (i.e., iron addition to diminishing H_2S emissions) are more expensive but also effective alternatives to control odor plumes (Gutiérrez et al., 2015a; Schlegelmilch et al., 2005).

3.4.2. Odorant contribution and odor quality

The OC profile along the composting process and the volatile compounds exhibiting OAV superior to one are depicted in Fig 8.A. Terpenes only occurred at concentrations above their ODT upon ADS storage. Likewise, ammonia could have contributed to odor annoyances during ADS storage and the earlier and middle active phase with OAV fluctuating from 2 to 21. Based on the OAV approach, VSC and acetic acid were generally the dominant odorous compounds for all composting stages. Notably, H_2S and acetic acid were the major odorants throughout the last operational stages of ADS composting. OAV

from H_2S emissions were closely correlated to OC (R^2= 0.81; $p<0.001$) for the later active phase and curing process as shown in Fig. 8A.

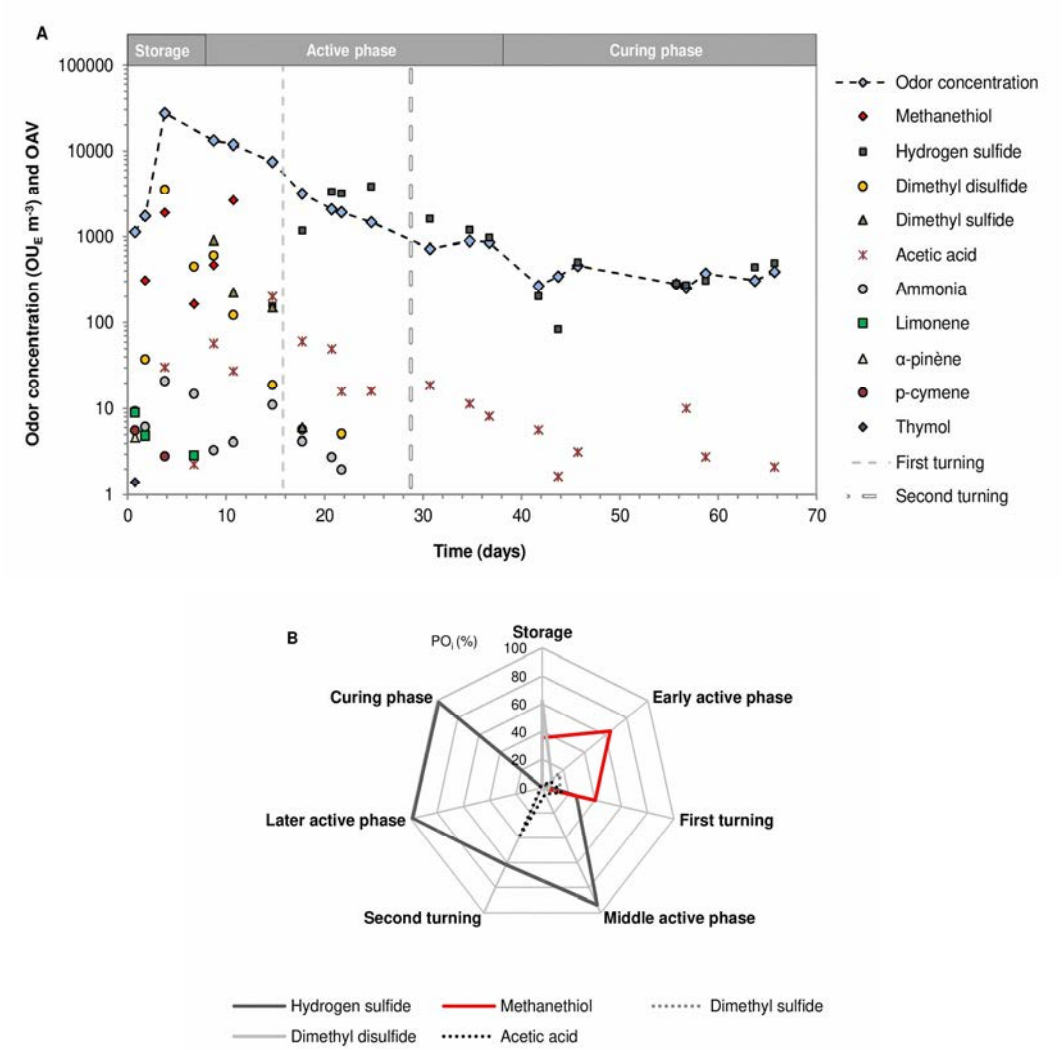


Fig. 8. Odor concentration (OC in OU_E m^{-3}) and odor activity values (OAV, dimensionless) profiles (**A**).Percentage of odor contribution (PO_i, %) for the major odor-causing compounds released throughout the different stages of ADS composting (**B**)

The main odorant composition patterns are summarized in Fig. 8B. Molecules' odor contribution (PO_i, %) were associated with specific odor descriptors to provide overall insight into the odor quality of gas exhausts from ADS composting. For instance, the odorous gas emissions produced when storing ADS were principally governed by DMDS (62%) and methanethiol (35%), commonly related to rotten-cabbage and garlic -like odors (Rosenfeld et al., 2007). This type of rotten-vegetable odor experience was similarly present during the earlier active composting phase and first turning where CH_3SH (64-40%) DMS (14-16%) and DMDS (4-9%) were the leading odorants. For the middle and later composting active phase, second turning, and curing process, a rotten-egg-like odor was perceived due to the occurrence of H_2S with PO_i ranging from 62 to 98 %. In the case of the second turning, the presence of acetic acid

(38%) could have added sour and rancid notes to the odor plumes. Understanding such odor descriptors can support and facilitate odor control and monitoring plans by providing intuitive and straightforward warns to plant workers about the generation of odor annoyances and exposure to hazardous chemical emissions.

4. Conclusions

Gas emissions from different composting operational stages of anaerobically digested sewage sludge (ADS) were investigated by analytical and sensory methods to understand the origin and causes of odor nuisances through this post-treatment. Among 19 volatile compounds quantified, ammonia and volatile sulfur compound (VSC) were targeted as the most abundant air pollutants. The active composting phase of ADS was the primary source of odor and air pollution, generating 77% of the net mass of compounds emitted and representing 82% of the overall odor emission factor (OEF). In particular, the first eight days of aerobic treatment were considerably involved in the release of odors (OEF: 6721 OU_E kg^1ADS) and contaminants (40% of compounds emitted). Similarly, the first turning process was responsible for strong odor emissions that were emitted in short lapse of time (295 $OU_E\,h^{-1}\,kg^{-1}ADS$).

Besides the earlier composting active phase and first turning, ADS storage also exhibited a significant odor nuisance potential with odor emission rates (OER) that increased by a factor of 10, reaching a maximum value of 17.6 $OU_E\ h^{-1}\ kg^{-1}ADS$. Based on the odor activity values (OAV) approach, dimethyl disulfide (DMDS), dimethyl sulfide (DMS) and methanethiol were identified as the main odorants through these early composting stages. Once the aerobic treatment proceeded and ADS was stabilized, there was a shift in the pattern of odorant composition and potential. For the middle and later active composting phase, the second turning and curing stage, OER values dropped (0.18-12.6 $OU_E\ h^{-1}\ kg^{-1}ADS$), and hydrogen sulfide constituted the most relevant odor-causing compound. All these odor patterns were chronologically differentiated and recognized by a PCA which explained 77 % of the variability in OC and OAV dataset, thus constituting a powerful data mining approach to facilitate odor monitoring in composting plants.

Finally, odor quality notions based on odorants contributions (PO_i, %) were provided to assist composting practitioners in diagnosing the occurrence of odor episodes along the different stages of ADS post-treatment straightforwardly.

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Supplementary material 1

Section 1. Physicochemical characterization of anaerobically digested sewage sludge (ADS)

Once sampled at the wastewater treatment plant (WWTP), ADS was characterized through different physicochemical methods. **Volumetric mass** was measured by weighing the fresh mass of ADS required to fill a plastic container of a known volume (11.43 L). The digestate was carefully placed inside this plastic container in order to avoid substrate compaction. **Dry matter** and **moisture content** were measured by drying from 2 to 3 Kg of ADS in triplicate at 80 °C until attaining a constant mass value. **Organic matter content** was assessed by the standard method NF U 44-160 (AFNOR, 1985), consisting of calcination at 550 °C of approximately 50 g of dried and shredded ADS. **Total carbon** was analyzed according to the standard method NF EN 13137 (AFNOR, 2001) in an Organic Elemental Analyzer Flash-2000 (ThermoFisherScientific). In this method, carbon was first oxidized to CO_2 by calcination at 1800 °C; CO_2 was then separated in a chromatographic column with helium as a carrier gas, and finally, CO_2 was quantified by a thermal conductivity detector (TCD). **Total Kjeldahl Nitrogen (TKN)** was quantified by the modified standard method NF ISO 11261 (AFNOR, 1995) involving the initial mineralization of the ADS with sulfuric acid (H_2SO_4, 18 M) to transform organic N into its ammoniacal form (NH_4^+/NH_3), followed by its steam distillation with NaOH (32%) and back-titration with H_2SO_4 (0.2 N) in an automated titration unit (Gerhardt Vapodest 50s). **Total ammonia nitrogen** (TAN or NH_4^+/NH_3) was determined by steam distillation with MgO, stripping into a boric acid trap (H_3BO_3, 40 g/L) and back-titrating with sulfuric acid (H_2SO_4, 0.2 N). **Chemical oxygen demand (COD)** was obtained by dichromate oxidation as described in NF T 90-101 (AFNOR, 2001).

Section 2. Emission profiles for main pollutants detected throughout composting of ADS

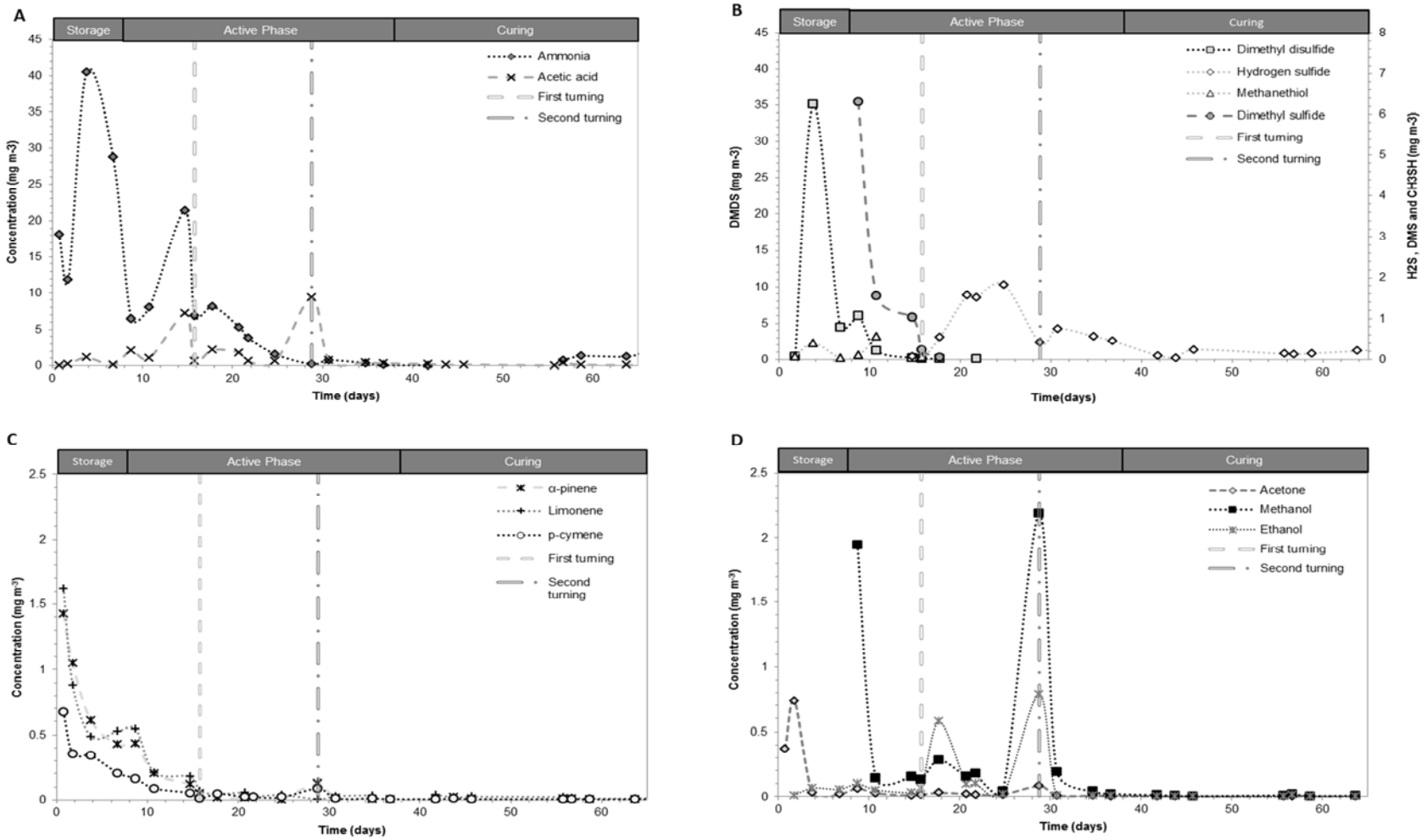


Fig. 1S. Emission profiles of main pollutants released upon composting of anaerobically digestated sewage sludge: ammonia and acetic acid (**A**), volatile sulfur compounds (**B**), terpenes (**C**) and oxygenated compounds (**D**)

Section 3. Ammonia and nitrous oxide emissions

Two ammonia peaks were detected within the first 15 days of composting simulation, followed by a continuous decrease on NH_3 levels. N_2O concentration peaked at 22nd day of the process while NH_3 dropped (Fig. 2S). ADS presented a low C/N of six and a significant initial content of NH_4^+/NH_3 because most of its organic nitrogen was extensively mineralized to free ammoniacal nitrogen (NH_4^+/NH_3) during anaerobic digestion (Zeng et al., 2016). This ammonia initially contained in ADS was likely volatilized under storage conditions, leading to the first NH_3 peak on the fourth day of storage. After starting the aerobic treatment, a second NH_3 peak was detected at the 15th days of the process that could be associated not only with NH_3 stripping but also with the increase of the biodegradation of organic nitrogen (ammonification) during the active composting phase. The decrease of NH_3 after this second peak was prompted by the stripping, microbial assimilation, and nitrification of NH_4^+/NH_3 (Arab and McCartney, 2017; Zeng et al., 2012). Nitrification and denitrification may have played a vital role on the N_2O emissions observed between the 11th and 25th day of aerobic treatment.

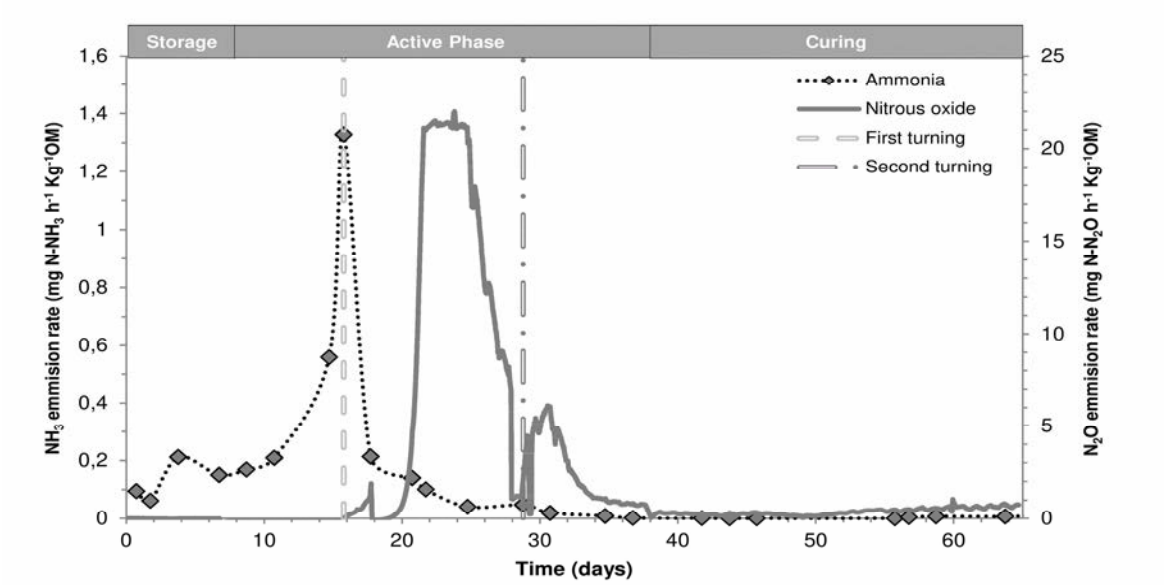


Fig. 2S. Emission rates for ammonia and nitrous oxide through different operational composting stages of ADS

Suplementary material 2 and 3

The datasets for chemical concentrations (Supplementary material 2), OC and OAV (Supplementary material 3) are published online as Mendeley datasets on the following link: http://dx.doi.org/10.17632/hch28xtj6b.1.

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Chapter 4: Chemical and odor characterization of gas emissions released during composting of solid wastes and digestates

Foreword

The composting active phase is considered as one of the critical process stages involved in odor and air pollutants emissions. Due to this, some efforts have been made to analyze the chemical and odor concentrations during the aerobic treatment of organic fraction of municipal solid waste (Maulini-Duran et al., 2013b; Scaglia et al., 2011; Schiavon et al., 2017), municipal solid waste (Eitzer, 1995; Rodríguez-Navas et al., 2012), food waste (FW) (Komilis et al., 2004), and sewage sludge (Durme et al., 1992; Maulini-Duran et al., 2013a). The large impact of the early days of composting active phase on odor emission was also underlined in Chapter 3. The results showed that a first OER peak during the first days of aerobic treatment of ADS but also high OEF values that remained constant over that process stage.

The first step to design and implement suitable odor and air pollution mitigation strategies is to characterize and understand the odor and chemical emission generation patterns of the emitting sources. Although some information can be found concerning odor and odorant emissions throughout the composting active phase, published results highly differ even for the same type of substrates treated due to the large variation on experimental and operational conditions, waste composition, and the employed analytical and instrumental methodology. Hence, the study of odors upon composting exhibits a limited systematic characterization that hinders the inter-comparison among studies at diverse treatment scales and the assessment of the real environmental impact of this waste recycling biotechnology.

In the light of these stated issues, the research work performed in Chapter 4 had a principal objective to characterize extensively the volatile compounds and odor emissions along the composting active phase of different solid wastes and digestates. This characterization was carried out under controlled experimental conditions that allowed establishing inter-comparison among the odor potential of different substrates, as well as providing reliable emission factors that could be eventually applied at larger scales. To this end, odors were monitored through dynamic olfactometry and instrumental-based methods. The main odor contributors from the gas sample were determined through an OAV approach. It is also worthwhile to mention that OEF were determined as a response to the lack of information observed in the literature.

The results obtained throughout the odor and chemical assessments demonstrated that the chemical composition and odor potential of gas emissions from composting was highly dependent on the origin and feedstock of composted wastes. Solid wastes were characterized for presenting more substantial odor and air pollutants emissions factors than anaerobically digested substrates. However, beyond the inherent odor potential of each substrate, the obtained results indicated that volatile sulfur compounds were the main drivers of odor nuisances for the composting process.

Chemical and odor characterization of gas emissions released during composting of solid wastes and digestates

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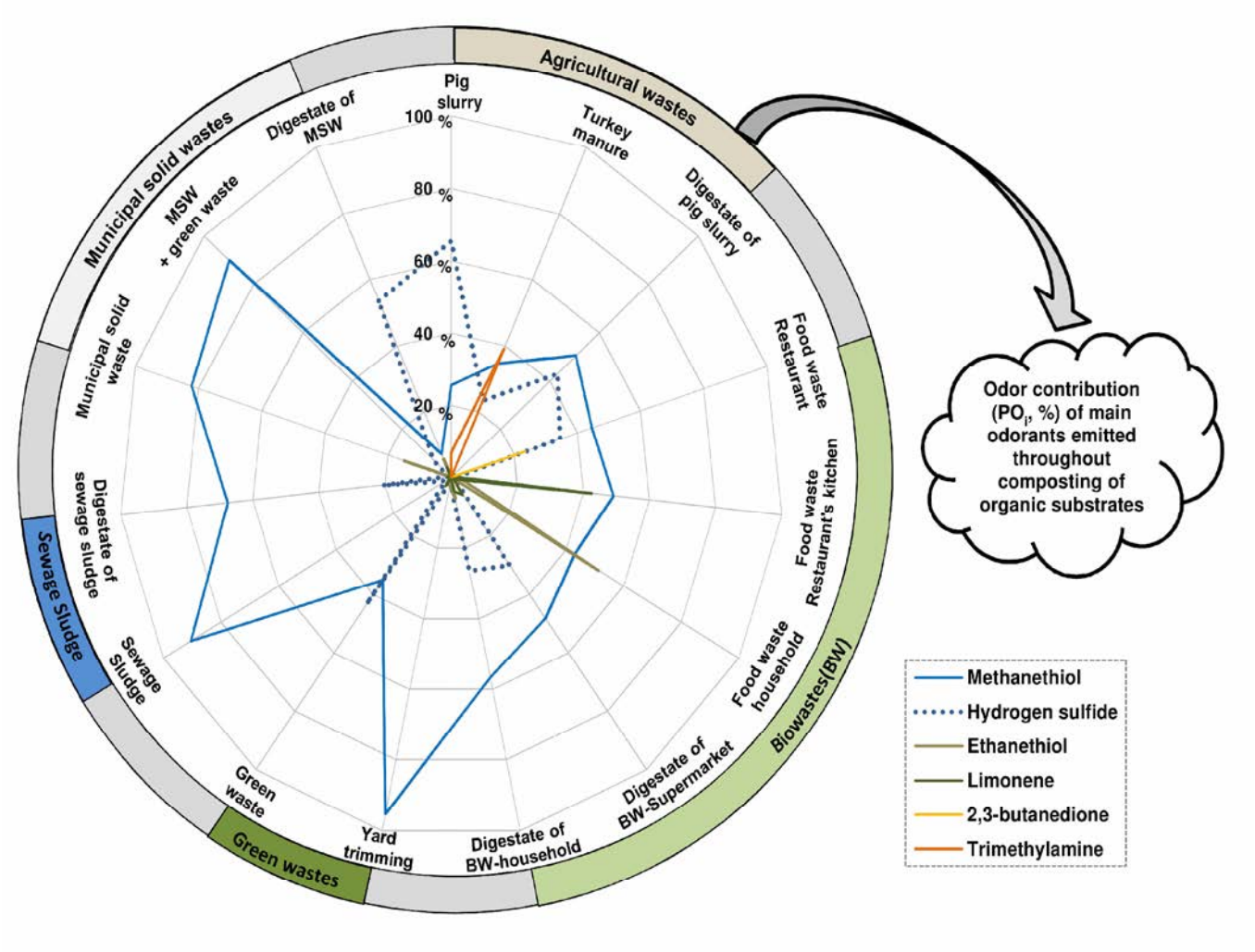
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Abstract

Hazardous and odorous gas emissions from composting and methanization plants are an issue of public concern. Odor and chemical monitoring are thus critical steps in providing suitable strategies for air pollution control at waste treatment units. In this study, 141 gas samples were extensively analyzed to characterize the odor and chemical emissions released upon the aerobic treatment of 10 raw substrates and five digestates. For this purpose, agricultural wastes, biowastes, green wastes, sewage sludge, and municipal solid waste (MSW) were composted in 300 L pilots under forced aeration. Gas exhausts were evaluated through dynamic olfactometry and analytical methods (i.e., GC/MS) to determine their odor concentration (OC in $OU_E\ m^{-3}$) and chemical composition. A total of 60 chemical compounds belonging to 9 chemical families were identified and quantified. Terpenes, oxygenated compounds, and ammonia exhibited the largest cumulative mass emission. Odor emission rates ($OU_E\ h^{-1}$) were computed based on OC measurements and related to the initial amount of organic matter composted and the process time to provide odor emission factors (OEF in $OU_E\ g^{-1}OM_0$). The composting process of solid wastes accounted for OEF ranging from 65 to 3089 $OU_E\ g^{-1}OM_0$, whereas digestates composting showed a lower odor emission potential with OEF fluctuating from 8.6 to 30.5 $OU_E\ g^{-1}OM_0$. Moreover, chemical concentrations of single compounds were weighted with their corresponding odor detection thresholds (ODT) to yield odor activities values (OAV) and odor contribution (PO_i, %). Volatile sulfur compounds were the main odorants (PO_i= 54-99%) regardless of the operational composting conditions or substrate treated. Notably, methanethiol was the leading odorant for 73% of the composting experiments.

Keywords: Forced aeration; odor emission factors; odor activity values; volatile sulfur compounds; methanethiol.

Graphical abstract



Highlights

- Terpenes, oxygenated compounds, and ammonia were actively emitted upon composting
- Odor emission factor (OEF) were computed for substrates treated
- Digestates composting exhibited lower odor emission potential than raw substrates
- An odor activity value (OAV) strategy was implemented
- Methanethiol and hydrogen sulfide were the major odor contributors along composting

1. Introduction

Moving toward better waste disposal is a key objective within the European Union framework. The EU environmental policies actively promote the implementation of wastes recycling biotechnologies such as composting and methanization (Directive 2008/98/EC). Composting process transforms organic wastes into a humus-like substance which is used as a soil conditioner in agricultural operations (Tambone et al., 2010). Before being spread on soils, anaerobically digested substrates (digestates) are also composted to stabilize their remaining organic matter content and remove possible harmful microorganisms (Zeng et al., 2012). Despite contributing to proper waste and digestate management, composting is a potential source of air and odor pollution. During this biological treatment, organic matter undergoes complex aerobic, anoxic and anaerobic metabolic reactions, resulting in the release of volatile organic compounds (VOC), greenhouse effect gases (CO_2, CH_4, and N_2O), ammonia and hydrogen sulfide (Krzymien et al., 1999; Y. Li Zhu et al., 2016).

The gas emissions released upon composting are commonly associated with odor annoyance and adverse health and environmental impacts (Scaglia et al., 2011). Odorous emission can produce nausea and psychological disturbances to plant-workers and communities located nearby waste treatment units (Müller et al., 2004). Malodors are the primary cause for neighbors complains at the surrounding areas of composting facilities (Schlegelmilch et al., 2005). Additionally, gas emissions from composting may contain considerable amounts of ammonia that can be toxic and aggravate acid rain phenomena and ecosystems eutrophication. Some carcinogenic and toxic substances can also be stripped under forced aeration treatments of municipal solid waste (Cadena et al., 2009).

A crucial step to implement suitable strategies for odor and air pollution abatement is to characterize the volatile compounds which are responsible for malodors and environmental hazards. The odorous gas samples are principally monitored by analytical and sensory methods (Capelli et al., 2008; Ueno et al., 2009). Dynamic olfactometry is the main sensory technique currently used in Europe to measure the odor concentration (OC in $OU_E\ m^{-3}$) (Laor et al., 2014). OC measurement consists of diluting a gas sample with odorless air to determine the dilution factor in which half of a calibrated human panel can perceive an odor stimulus (EN 13725, 2003). In contrast, analytical methods focus on evaluating and quantifying the chemical composition through instrumental-based techniques such as GC/MS, gas tubes and wet methods (scrubbers and traps)(Blanes-Vidal et al., 2009; Blazy et al., 2014a; Tsai et al., 2008). Particularly, CG/MS coupled to pre-concentration techniques such as solid phase microextraction (SPME), and thermal desorption tubes are commonly employed for determining VOC with great sensibility and accuracy (Laor et al., 2014). Such pre-concentration step onto a sorbent material is required to warrant the detection of analytes present in the ambient air at low concentrations (Font et al., 2011).

The principal advantage of using instrumental means to assess odors lies in determining the major odor contributors from complex gas mixtures of volatile compounds (Gallego et al., 2012). Compounds chemical concentrations can be weighted with their corresponding odor detection thresholds (ODT) to identify the substances exceeding the odor perception limits. ODT is defined as the compounds chemical concentration at which 50% of a studied population distinguishes an olfactory stimulus from odorless gas (Capelli et al., 2008). Precisely, the ratio between the chemical concentration of a single compound to its ODT is known as odor activity value (OAV) and has been widely employed for odorants monitoring in composting gas emission (Blazy et al., 2015; Fang et al., 2013; Schiavon et al., 2017; Y. Li Zhu et al., 2016). OAV is a dimensionless parameter used as an odor surrogate to identify the odorous potential of each substance contained in a gas sample (Laor et al., 2014). In theory, molecules exhibiting the highest OAV are the ones that contribute the most to odor nuisances (Parker et al., 2012). However, this odor monitoring approach presents two clear limitations: i) the considerable variability among ODT found in the literature and ii) the omission in the OAV calculation of possible interactions among odorous molecules which may produce synergistic, antagonistic or even neutralizing effect when perceiving odorous gases (Parker et al., 2012; Wu et al., 2015).

Generally, most of the studies related to composting gas emissions are focus on VOC and odor characterization upon treatment of specific organic matrices such as organic fraction of selected municipal solid waste (OFMSW) (Maulini-Duran et al., 2013b; Scaglia et al., 2011; Schiavon et al., 2017), municipal solid waste (MSW) (Eitzer, 1995; Rodríguez-Navas et al., 2012), food waste (FW) (Komilis et al., 2004), and sewage sludge (SS) (Durme et al., 1992; Maulini-Duran et al., 2013a). Only a few numbers of studies have been addressed toward the analysis of odorous and gaseous pollutants emitted when composting digestates and their comparability with raw substrates (Maulini-Duran et al., 2013a; Pagans et al., 2006b; Zeng et al., 2016). Moreover, comparisons among gas emission data are frequently hindered by the differences in studies scales, process conditions, and means to express concentrations (Cadena et al., 2009).

Volatile sulfur compounds (VSC) also occur in gas emissions from the aerobic treatment of MSW (Zhang et al., 2013), SS (Maulini-Duran et al., 2013a; Y. Li Zhu et al., 2016) and FW (Mao et al., 2006). These compounds are produced by anaerobic metabolism of organic matter within anaerobic pockets and clumps formed as a result of waste nature (i.e., high moisture content and low porosity) and composting conditions (Higgins et al., 2006; Maulini-Duran et al., 2013a). VSC must be integrated to odor and chemical monitoring in composting studies as they are toxic and easily perceived at extremely low concentrations (Rosenfeld et al., 2007). In fact, VSC are usually regarded as the primary target compounds when assessing odors along composting operations (He et al., 2018; Zhang et al., 2013).

Given the need for more accurate and comprehensive information on gas emissions and odors from the aerobic treatment of various organic matrices, the present study extensively characterized the volatile

compounds and odor emissions upon composting of different digestates and solid wastes. For this purpose, ten solid wastes and five digestates were composted in pilot-scale reactors of 300 L. A total of 141 gas samples were collected and analyzed by GC/MS, GC/electrochemical detection, and acid traps to yield cumulative mass emissions and chemical composition profiles of VOC, VSC, and ammonia. Furthermore, an odor monitoring strategy based on OC measurement and OAV calculation was adopted to determine the odor emission rates (OER), odor emission factors (OEF) and the major odor contributors throughout the aerobic treatments. ODT from 15 volatile compounds were measured by dynamic olfactometry to minimize possible drawbacks from using highly variable ODT datasets found in the literature.

2. Materials and methods

2.1. Substrates collection and storage

Ten solid wastes and five anaerobically digestated substrates (AD) were collected from 13 sites in France over a time span of 14 months. Organic matrices were classified as agricultural wastes, municipal solid wastes, biowastes, sewage sludge, and green wastes according to the waste compositions and origins. Table 1 shows the substrates classification and origins in addition to any possible treatment applied to the samples before collection. Once sampled, the substrates were rapidly stored in plastic bags at -18 °C during two or three weeks. Two days before running the composting experiments, frozen substrates were thawed at room temperature. The physicochemical characteristics of each composted substrate are detailed in Supplementary material (Table 1S).

Table 1. Collected substrates: composition and origins

Type of waste	Substrate[a]	Sampling place[b]	Plant feedstock/substrate composition	Pre-treatment[c]	Acronyms
Agricultural wastes	Pig Slurry	Pig farm	Solid fraction of pig slurry	Solid-Liquid separation	SPS
	Turkey Manure	Turkey farm	Humidified poultry manure	-	TM
	Solid fraction of AD pig slurry	Pig farm	Pig slurry (49.6%), food waste (35.5%) and green waste (14.9%)	Wet digestion at 40°C Centrifugation	ADP
Biowastes	Food waste	Restaurant	Fruits and cooked vegetables, meat, pasta, bread, grease, and fish	-	FWR
	Food waste	Restaurant's kitchen	Fruit and vegetable peelings, grease, and coffee ground	-	FWK
	Household food waste	CoP	Fruit and vegetable peelings, paper, grease, bread, coffee ground, cooked and raw vegetables, meat, pasta, and bread	-	FWH
	Solid fraction of AD biowaste	MeP	Biowaste of hypermarkets (60%), grease from the food industry (28%), and cereals wastes (12%)	Wet digestion at 40 and 20 °C Screw press	ADB
	Solid fraction of AD biowaste	MeP	Household biowastes (72%), restaurant biowastes (12%), and green biowaste (12%)	Dry digestion at 55°C Screw press	ADH
Green wastes (GW)	Yard trimming	Green area	Leaves, grass, and brush	-	YT
	Green wastes	MeP	Green waste (52%), household biowaste (42%), markets biowaste (2.6%), and restaurant biowastes (2.4%)	Mechanical sorting Mixing and ground	GB
Sewage sludge	Sewage sludge	CoP	Secondary sludge from WWTP	-	SS
	Solid fraction of AD sewage sludge	WWTP	Secondary sludge from WWTP	Wet digestion at 37.5 and 20 °C Centrifugation	ADS
Municipal solid wastes	OFMSW	MSWTP	Food waste, paper, cardboard, sanitary textiles, and plastic films	Pre-fermentation in rotating drums Mechanical sorting	MSW
	OFMSW+ GW	MSWTP	Food waste, paper, cardboard, sanitary textiles, plastic films, and green waste	Pre-fermentation in rotating drums Mechanical sorting	MSG
	Solid fraction of AD OFMSW+GW	MSWTP	Food waste, paper, cardboard, sanitary textiles, plastic films, and green waste	Dry digestion at 40 °C	ADM

[a] AD: anaerobically digested, OFMSW: organic fraction of municipal solid waste, GW: green wastes.
[b] CoP**:** dumping area of composting plants, MeP**:** methanisation plants, WWTP: wastewater treatment plants, MSWTP**:** municipal solid waste treatment plants.
[c] **-:** no pre-treatment.

2.2. Experimental set-up

Composting process was simulated in 300 L reactors along five experimental campaigns from April 2016 to June 2017. Composting reactors were thermally isolated by 10 cm polyurethane layers. Each experiment consisted of the aerobic treatment during approximately 31 days of 3 different substrates in airtight-stainless steel reactors mechanically supplied with forced air. The air inflow was regulated by a rotameter (FL-821-V, OMEGA Engineering Inc.) and a volumetric gas meter (Gallus 2000, Actaris, Liberty Lake) daily measured. Temperature and weight were continuously monitored by using 4 Pt100 probes and mass sensors (X201-B, PRECIA MOLEN). Composting reactors were covered by metallic cone-shaped lids containing a gas outlet and a gutter to collect water condensates. The exhaust air stream was first channeled to a bottle condenser to remove any water vapor excess and then conveyed toward an acid traps system, gas analyzer, and gas sampling point. Concentrations of oxygen at the air inflow and outflow were analyzed by a paramagnetic analyzer (Magnos 206, ABB, Zurich, Switzerland). The dry-air molar flow rate was expected to remain constant along the system. The molar outflow rate of water vapor was then calculated by assuming that gas exhaust was water-saturated (Blazy et al., 2014b). The difference of O_2 concentration at the reactor's inlet and outlet allowed computing the oxygen uptake rate (OUR in $gO_2\ h^{-1}\ kg^{-1}OM_0$) (de Guardia et al., 2010a; Scaglia et al., 2011). A detailed scheme and description of the composting device are given by Blazy et al. (2014b).

Solid wastes and digestates were mixed, if needed, with oak wood chips with a particle size inferior to 40 mm to improve substrates bulking density. The mixing ratios bulking agent (BA) to substrates on a fresh mass basis ranged from 0.4 to 1.1 (Table 2). Once loaded, the compostable mixtures were firstly aerated for 24 to 48 h with a mean aeration flow ranging from 94.3 to 194.6 L h^{-1} to raise the temperature gradually and prevent a possible cooling of the composting pile caused by excessive aeration (Zeng et al., 2016). This initial material conditioning was followed by setting up the aeration rates to experimental values that were maintained constant during the entire experiment (Table 2). The aeration rates were selected on the basis of the real-scale composting conditions at the sampling sites and prior studies (de Guardia et al., 2010a). Table 2 provides the experimental conditions and mixtures compositions used in this research work. Compostable mixtures were turned twice by emptying the reactors, mixing their load, and refilling the composting devices. Turning was usually performed after 10 and 20 days of the process.

Table 2. Mixtures compositions and composting conditions

	Compostable substrate														
Mixture composition	**SPS**	**TM**	**ADP**	**FWR**	**FWK**	**FWH**	**ADB**	**ADH**	**YT**	**GB**	**SS**	**ADS**	**MSW**	**MSG**	**ADM**
Substrate fresh mass (Kg)	147.6	135.1	126.3	79.9	87.6	55.1	97.9	82.6	47.6	91.2	72.7	81.0	78.0	68.6	75.7
OM_0 content (%FW)	22.8	25.2	24.2	25.9	18.3	28.4	19.1	24.7	16.4	26.6	11.6	10.5	32.9	32.3	16.8
BA fresh mass (kg)	0.0	0.0	0.0	57.1	43.3	48.7	69.0	58.3	43.8	0.0	78.6	41.5	34.2	74.3	75.1
Water added (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.0	45.0	0.0	0.0
Ratio BA/S	0.0	0.0	0.0	0.7	0.5	0.9	0.7	0.7	0.9	0.0	1.1	0.5	0.4	1.1	1.0
Mixture moisture (%)	68.5	68.8	62.5	49.3	59.3	44.6	69.3	41.9	50.0	53.7	49.4	62.6	60.1	35.1	43.4
Experimental conditions															
Mean aeration rate ($L\ h^{-1}\ Kg^{-1}$)	1.2	1.4	3.0	5.3	3.6	4.6	1.9	1.7	2.7	4.0	5.0	3.9	4.3	6.4	2.6
Turning date[a] (days)	14/24	14/24	10/20	10/21	10/21	10/20	14/24	10/21	10/21	9/21	10/20	10/21	10/21	9/21	9/21
Process duration (days)	31.6	31.6	30.9	31.7	31.7	30.9	31.6	31.7	30.7	30.8	30.9	31.6	30.7	30.8	30.8

%FW: percentage in fresh weight; OM_0: initial organic matter content; BA: bulking agent; BA/S: ratio BA to substrate on a fresh mass basis.
[a] Turning date: i.e., the composting mixture was turned at 14 and 24 days of the process

2.3. Gas sampling and chemical analysis

For each substrate, gas samples were taken three times per week along the composting campaigns. A total of 141 gas samples from composting process were collected at room pressure and temperature into 30 L single-use nalophan bags by following the EN13725 recommendations for sampling in channeled sources (EN 13725, 2003). Due to chemical compounds lability, adsorption process onto carbotraps, sulfide compounds analysis, and olfactometric assessment were shortly conducted within 1 to 6 hours of the sample collection. Minimizing storage time prevented compounds losses owing to collateral chemical reactions and permeability onto the nalophan bag surface (Mochalski et al., 2009).

2.3.1. Ammonia analysis

Two glass impingers filled with 200 mL of sulfuric acid (H_2SO_4 1 N) were set and connected in series to absorb ammonia vapors coming from the air exhaust stream. The pilot's outflows were continuously controlled and measured by a flow meter (FL-821-V, OMEGA Engineering Inc.) and a volumetric gas counter (Gallus 2000, Actaris, Liberty Lake). Acid traps were changed every 48 hours. Ammonia (NH_4^+/NH_3) adsorbed into acid solutions was released by steam distillation with sodium hydroxide (NaOH, 32%) and taken into boric acid solution (H_3BO_3, 40 g L^{-1}) according to the modified method NFT 90-015-1. An automated distillation/titration system (Gerhardt Vadopest 50s, Germany) quantified collected ammonia steam with H_2SO_4 (0.2 N) as a titrant agent. Only duplicated measurements with variance coefficients below 5% were considered in this study. The method detection limit (MDL) for ammonia was 0.286 mg m^{-3}.

2.3.2. Volatile organic compounds (VOC) quantification

VOC were determined by GC/MS coupled to thermal desorption unit (TD-GC/MS) following a previously optimized method for gas emission from pig slaughterhouse sludge composting (Blazy et al., 2015). Gas samples collected in nalophan bags were adsorbed and concentrated onto carbotraps (Carbotraps 349, Perkin Elmer, USA) using a calibrated vacuum pump (Gilair3, USA) with a mean gas flow rate of 52 mL min^{-1}. Three different volumes (~50, 250, and 500 mL) of each gas samples were generally pre-concentrated onto individual carbotraps to ensure the evaluation of VOC at diverse concentration ranges. A thermal desorption unit (TurboMatrix 550, Perkin Elmer) released adsorbed VOC (primary desorption at 200°C for 5 min and inner cold trap desorption at 180°C for 5 min) and swept them on a nitrogen (N_2) flow rate of 50 mL min^{-1} toward a gas chromatographer coupled to a mass spectrometer (Clarus 500 GC-MS, Perkin Elmer, USA). Once injected, VOC were eluted through a capillary column CP-WAX 58 (25m x 0.15 mm x 0.25µm, Varian, USA) with a helium flow of 1 mL min^{-1}

as a carrier gas and a column pressure of 310 kPa. The oven GC temperature was first held at 40 °C for 5 min, then ramped to 180 °C at 10°C min^{-1} and finally kept at 180 °C for 5 min.

Separated VOC were scanned into a quadrupole mass spectrometer detector acquiring from 20 to 300 amu (atomic mass unit) every 1.5 s. Compounds were identified by comparing obtained mass spectra with reference entries from a spectral mass library (NIST 2012, National Institute of Standards and Technology, USA). Additionally, retention times of standard compounds were also used as references for analytes identification. Spectra base peaks were monitored and integrated into a full scan and SIR (Specific Ion Recording) mode. An external calibration process (R^2= 0.92-0.99) enabled to quantify target VOC with pure chemical compounds (Purity > 98%, suppliers: Fluka, Fisher, Janssen Chemical, Sigma Aldrich, Acros Organic and Alfa Aesar). Some quality assurance (QA) parameters such as the limit of detection (LOD), limit of quantification (LOQ), and calibrations coefficients are listed in Table 4. LOD was determined by linear extrapolation of the minimum standard quantity to find a ratio signal to noise equal to 3, while LOQ was obtained by considering a ratio signal to noise equal to 9 (Defoer et al., 2002; Mochalski et al., 2009). Not calibrated compounds were semi-quantified by taking into account an average coefficient response equal to 1000.

2.3.3. Volatile sulfur compounds (VSC) quantification

Sulfur species were analyzed and quantified by a micro GC coupled to an electrochemical detector (airMEDOR, Chromatotec, France) according to the norm ISO 6326-2 (1981). The target compounds were hydrogen sulfide (H_2S), methanethiol (CH_3SH), ethanethiol (CH_3CH_2SH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). A gas pump filled a sample loop of 400 µL with the collected gas samples at 100 mL min^{-1}. Looped gases were then carried into a capillary column (1.2 m x 1.6 mm x 180 µm) kept at 40 °C with an air flow of 4 mL min^{-1} and a column pressure of 230 hPa. The separated sulfide compounds reacted with a chromic oxide solution (CrO_3, 10%) in an electrochemical cell composed of two platinum electrodes. External calibration and internal calibration were used to quantify VSC (R^2= 0.94-0.99) with high purity compounds (chemical purity> 98.5%, suppliers: Sigma-Aldrich and Acros organics; H_2S and CH_3SH standards at 200 ppm supplied by Air Liquide). The LOQ ranged from 0.006 to 0.024 ng (Table 4). LOQ was calculated by extrapolating the minimum area possibly measured by MEDOR (1000 unit area) into the performed calibration curves.

The cumulative mass production of VOC, ammonia, and VSC along composting process were expressed as a ratio of the initial organic matter content of substrates (OM_0) for a constant aeration flow (Supplementary material, Table 2S). The chemical contribution (PC_i, Wu et al. 2017) of the identified chemical families and compounds was calculated on a percentage basis as follows:

$$PC_i = \frac{\sum C_i}{\sum C_t} * 100\% \quad \text{Eq.1}$$

Where $\sum C_i$ is the cumulative mass production of a specific compound or chemical family (mg $Kg^{-1}OM_0$), and $\sum C_t$ is the net production of volatile compounds (mg $Kg^{-1}OM_0$).

2.4. Sensory measurements and odor activity values (OAV)

2.4.1. Odor concentration (OC) and odor emission rates (OER)

Gas samples collected during composting of 14 organic matrices were assessed by dynamic olfactometry according to EN 13725 guidelines. Odor concentration in European odor units ($OU_E\ m^{-3}$) and ODT of chemical standards were measured in a forced-choice, dynamic dilution olfactometer accounting for eight panelists single ports (ONOSE 8, Consumaj, Canada). The dynamic olfactometer is equipped with calibrated air mass flow controllers that deliver precise dry air and sample volumes with a low reading error ranging from 0.2% to 1%. For extremely high odorous emissions, gas samples were pre-diluted 100 folds by using a tight gas syringe (SGE, Australia) (Blazy et al., 2015).

The OC measurement consisted of evaluating the dilution factor in which half of a calibrated odor panel perceived a diluted gas sample. A total of 15 human subjects were selected according to their sensibility to n-butanol (Sigma-Aldrich 99.9%). Pre-diluted or raw gas samples were first diluted with odorless dry air to levels not detectable by a panel comprising a minimum of five assessors. Diluted gas samples were then presented in an ascending concentration order by reducing the dilution rate in a step factor of two until all panelist perceived odors. ONOSE 8 produced precisely dilutions factors ranging from 53333 to 6.5 ($2^{2.7}$-$2^{15.7}$) within a time response inferior to 10 s. Odor detectability at each dilution factor was assessed in a forced-choice mode involving the identification of an odor stimulus from odorless gas in a three-port sniffing station. According to EN 13725 (2003), the dilution factor at the odor detection threshold (Z_{50}) is equal to OC for standard conditions. The range of dilutions was presented three times for each gas samples. However, only individual threshold estimates from the two last presentations were used to calculate the Z_{50} geometric mean. Additionally, results from duplicates or triplicates at each sampling day were averaged to yield the final OC geometric means.

The odor emission rates (OER in $OU_E\ h^{-1}$) were calculated as a product of the OC geometric mean from the tested replicates ($OU_E\ m^{-3}$) and the mean outflow rates ($m^3\ h^{-1}$). OER was reported as a ratio of the initial organic matter content ($OU_E\ h^{-1}\ kg^{-1}OM_0$). Moreover, the odor emission factor (OEF) or cumulative OC was obtained by integration of OER throughout the composting time (Sironi et al., 2006). OEF is a term analogous to the emission factor which links the overall quantity of odor produced to the amount of substrate composted ($OU_E\ g^{-1}OM_0$).

2.4.2. Odor detection thresholds (ODT)

The Z_{50} for high purity compounds (>99.9%) and gas standards was determined following the same procedure than for OC assessment of composting gas exhaust. To this end, gas samples of 15 compounds were prepared in duplicate or triplicate by injecting a known volume of the standard into nalophan bags containing 30 L of odorless dry air. The injected substances were then volatilized at room temperature during one to three hours before conducting the olfactometric analysis. The initial compound concentrations in the prepared gas samples ranged from 0.4 to 404 mg m^{-3} (Supplementary material, Table 3S). These theoretical concentrations were calculated as the ratio of the mass injected (using compounds' densities) to the final gas sample volume. Previous studies have demonstrated that some compounds can be adsorbed and diffused onto the nalophan bag's surface and react with other molecules during storage (Kasper et al., 2018; Hansen et al., 2012), leading to a decrease on odorants concentrations. Therefore, the exposure concentration (C_0, mg m^{-3}) at the time of sensory analysis was determined by considering the relative losses of analyzed substances within the storage time (Supplementary material, Table 3S). Such relative losses were evaluated through GC/MS, and GC coupled to electrochemical detection but also employing the reported compounds recoveries from literature (Hansen et al., 2012; Sironi et al., 2014). Once Z_{50} was assessed for each gas bags, the odor detection threshold of the tested compound (ODT_i) were computed through Eq. 2.

$$ODT_i = \frac{C_0}{Z_{50}} \quad \text{Eq. 2}$$

2.4.3. OAV and odor contribution (PO_i)

OAV were calculated as the ratio of the compounds chemical concentrations to their odor detection thresholds. The highest OAV (OAV_{max}) along the entire process provided valuable information about the odorants contributing the most to odor nuisance (Blazy et al., 2014a; Gallego et al., 2012). Hence, the OAV_{max} for each quantified chemical substance and family was compared to the sum of all determined OAV_{max} ($SOAV_{max}$) to yield the percentage of odor contribution (PO_i, Wu et al. 2017), as shown in Eq. 3:

$$PO_i = \frac{OAV_{max-i}}{SOAV_{max}} * 100\% \quad \text{Eq.3}$$

3. Results and discussion

3.1. Composting performance and odors

3.1.1. Temperature and oxygen uptake rates (OUR)

Temperature profiles obtained upon composting of solid wastes and digestates are depicted in Fig. 1. The temperature rise was highly influenced by the substrate nature and the operational composting conditions; yet, some general trends were observed. For all treated substrates, the mean temperature of composting piles typically increased during the first 15 days of aerobic treatment as a result of the intense organic matter degradation by microorganisms (de Guardia et al., 2010a). For these first 15 days of forced aeration treatment, the composting piles reached maximum temperatures that ranged from 44 to 69 °C. ADM showed a maximum temperature of 34 °C (Fig. 1E), probably because this organic matrix had already been subjected to anaerobic digestion that lowered its biodegradability potential (Maulini-Duran et al., 2013a). Additionally, an upward temperature trend was typically evidenced once the composting pile was aerated and redistributed inside the pilot through the turning process. Turning improved porosity of compostable mixtures and made oxygen accessible for zones not previously supplied with O_2. Finally, the temperature generally dropped from 21 to 38 °C by the end of the forced aeration treatment, except for FWR which still exhibited a final temperature of 42 °C (Fig. 1D). Such a decrease on temperatures was caused by the decline of the microbial activity and substrates stabilization along the last days of aerobic treatment.

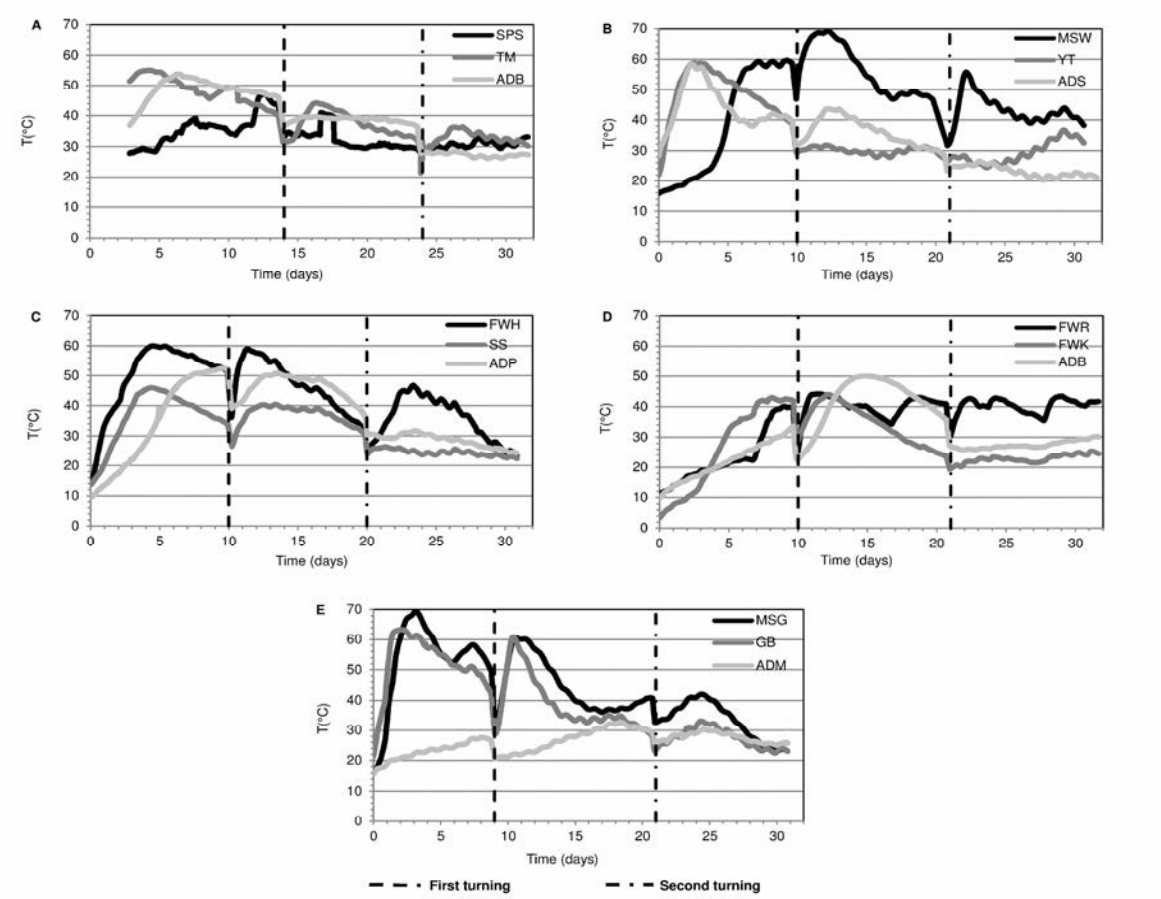


Fig. 1. Temperature (T,°C) profiles for solid waste and digestates composting

Table 3 provides a summary of the maximum and final composting pile temperature and the oxygen uptake rates (OUR). The OUR profiles for each composted substrates are also presented in supplementary material (Fig. 1S). OUR profiles generally followed the same trend than temperature; that is, oxygen consumption rate rose at the beginning of the forced aeration treatment and then decreased as the composting process proceeded. OUR_{max} was commonly detected within the first 17th days of the process (Table 3). The mean OUR for the last day of the process was also computed to evaluate the level of stabilization of composted substrates. De Guardia et al. (2010a) and Adani et al. (2004) proposed an OUR_{final} of 0.5 $gO_2\ h^{-1}\ Kg^{-1}OM_0$ as a criterion for stable compost. Except for FWR and SPS, all substrates exhibited OUR_{final} close or below this stabilization criterion (Table 3). OUR_{final} for FWR was not low enough (5.8 $gO_2\ h^{-1}\ Kg^{-1}OM_0$), thus suggesting that this raw substrate was not stabilized and required a longer aerobic treatment, the application of a higher aeration rate or the use of larger wood chips to substrate ratio. Even if SPS showed a rather suitable temperature profile (Fig. 1A), this agricultural waste was not fully stabilized as proved by its OUR_{final} of 1.6 $gO_2\ h^{-1}\ Kg^{-1}OM_0$. SPS was composted under low aeration rates without bulking agent addition which may explain the need for a more extended composting time. Although the composting conditions for FWR and SPS did not enable their final stabilization, their odor emissions were still assessed because they provide insight into the least favorable scenario while approaching to real composting conditions in the sampling sites.

Table 3. Biological stabilization parameters obtained along composting of solid wastes and digestates

Type of waste	Substrate	OUR_{max}[a] ($gO_2\ h^{-1}\ Kg^{-1}OM_0$)	OUR_{final}[b] ($gO_2\ h^{-1}\ Kg^{-1}OM_0$)	T_{max} (°C)	T_{final} (°C)
Agricultural	SPS	1.81 (12.6)	1.60	47.38	33.15
wastes	TM	2.35 (14.1)	0.22	55.11	30.17
	ADP	2.21 (10.7)	0.06	52.40	24.18
Biowastes	FWR	6.22 (26)	5.81	44.22	41.69
	FWK	4.59 (6.8)	0.27	43.94	24.43
	FWH	2.9 (10.7)	0.14	59.96	23.41
	ADB	2.74 (17.7)	0.24	53.84	27.31
	ADH	2.37(1.8)	0.34	50.00	30.11
Green wastes	YT	4.46 (1.72)	0.69	58.79	32.47
(GW)	GB	1.59 (0.8)	0.03	63.38	23.11
Sewage sludge	SS	6.43(2.1)	0.30	45.60	22.35
	ADS	6.71 (2.3)	0.29	58.42	21.05
Municipal solid	MSW	3.85 (6.9)	0.39	69.30	38.22
wastes	MSG	2.26 (0.9)	0.07	69.40	23.19
	ADM	1.95(0.9)	0.11	32.66	25.69

[a]OUR_{max}: Maximum oxygen uptake rate; in parentheses the process days when OUR_{max} was detected.

[b]OUR_{final}: Mean oxygen uptake rate at the final day of treatment.

3.1.2. Odor emission rates (OER) and odor emission factors (OEF)

OER profiles for 14 substrates composted are illustrated in Fig. 2. OER increased during the first 15 days of the aerobic process, coinciding with the thermophilic phase in which most of the readily available organic matter is broken down by microorganisms. The maximum OER for the studied raw substrates ranged from 829 to 27306 $OU_E\ h^{-1}\ kg^{-1}OM_0$, whereas digestates exhibited maximum OER that fluctuated from 22 to 115 $OU_E\ h^{-1}\ kg^{-1}OM_0$ (Fig. 2). The OER rise during the first two weeks of the active composting phase has been similarly described upon the aerobic treatment of OFMSW, sewage sludge, horticultural wastes and biowastes (Gutiérrez et al., 2015, 2017a; Schlegelmilch et al., 2005). During this intense stage of microbial activity, organic matter undergoes an onset of anaerobic, aerobic and anoxic transformations leading to the release of potential odorants (Gutiérrez et al., 2017b; Scaglia et al., 2011). Additionally, the stripping of embed volatile compounds into the organic matrices by the forced aeration treatment plays a vital role in the occurrence of odorous compounds (Staley et al., 2006). Except for FWR, OER dropped to values that ranged from 2.6 to 45.5 $OU_E\ h^{-1}\ kg^{-1}OM_0$ during the last day of the process when organic matrices were already composted. OER peak for FWR occurred at 24 days of the process because it was not fully stabilized at that time by the applied aerobic treatment (Fig. 2D).

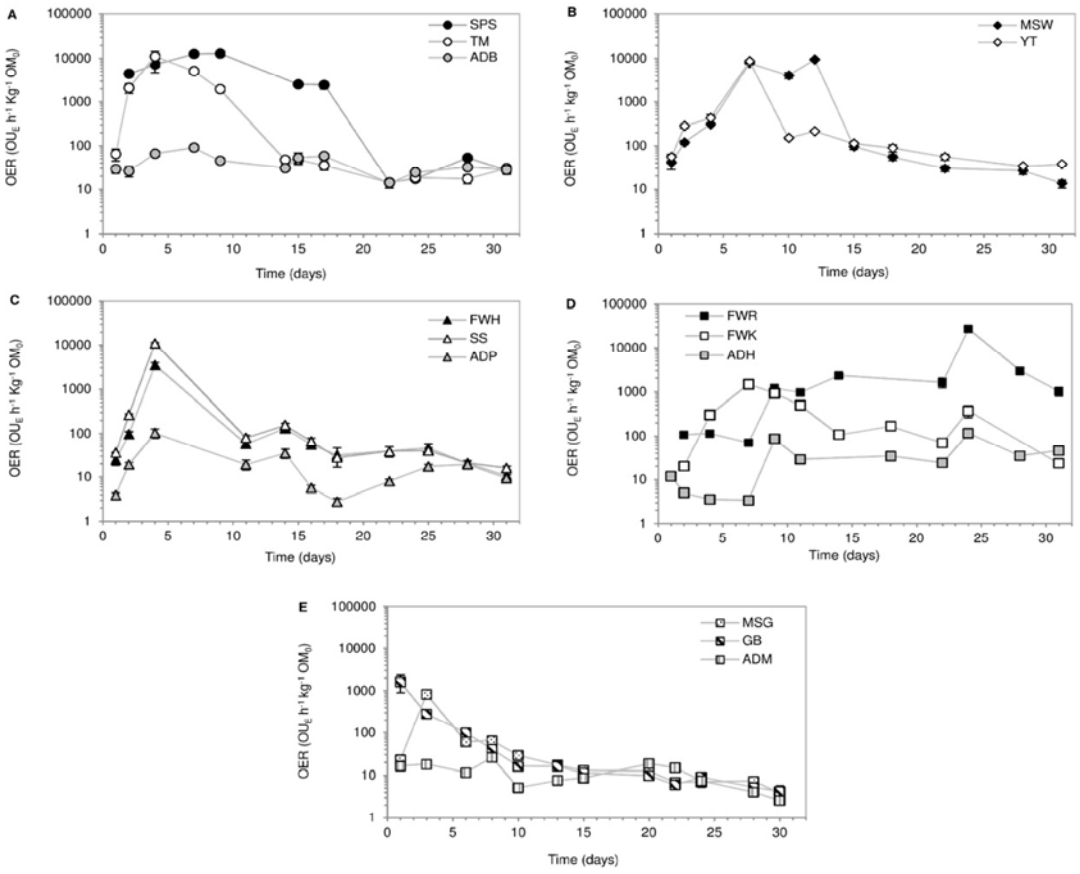


Fig. 2. Odor emission rates (OER in OU_E h^{-1} kg^{-1} OM) for solid wastes and digestates composting

The upward trend in OER during the first days of the process was less marked for digestates than for solid wastes (Fig. 2). Digestates were partially stabilized by anaerobic digestion, thus reducing the emission potential of odorants released through their aerobic degradation. Besides accounting for a higher degree of stabilization, digestates were typically composted with wood chips that decreased the amount of readily degradable organic matter present in the compostable mixture (Maulini-Duran et al., 2013a) and reduced the occurrence of anaerobic zones commonly related with odorant emissions.

The odor emission factors (OEF in OU_E $g^{-1}OM_0$) obtained during composting of 14 substrates are provided in Supplementary material (Table 2S) and depicted in Fig. 3. OEF linked the overall odor impact and quantity of released gas emissions with the amount of substrate composted. The composting process of solid wastes accounted for significant OEF ranging from 3089 to 65 OU_E $g^{-1}OM_0$, while digestates composting showed lower OEF that varied from 30.5 to 8.6 OU_E $g^{-1}OM_0$. Hence, applying a combined anaerobic-aerobic treatment could drastically reduce the odor offensiveness of emissions generated along the stabilization process of raw materials. For instance, OEF obtained upon composting of ADP was 137 times inferior to OEF values from SPS composting (Fig. 3). In line with our results, Shiavon et al. (2017) recommended the use of an anaerobic digestion step prior composting to enhance the energetic valorization of wastes and control odor emissions.

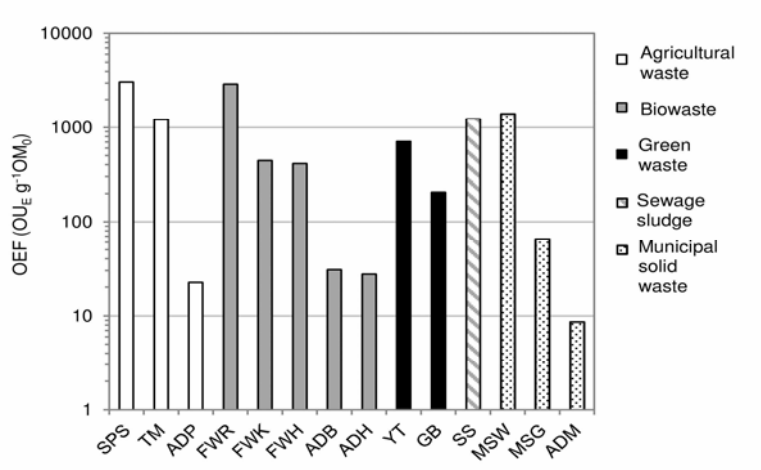


Fig. 3. Odor emission factors (OEF in $OU_E\ g^{-1}OM_0$) obtained upon aerobic treatment of solid wastes and digestates

Under the employed composting conditions, SPS and FWR exhibited the maximum OEF. Such substrates were treated with a limited oxygen supply, probably reflected in the formation of anaerobic zones and production of odorous compounds. Likewise, other authors have associated food waste composting with strong odor episodes due to the high moisture content and low biological stability of this organic matrix (Schiavon et al., 2017; Tsai et al., 2008).

The odor emission potential of TM, SS and MSW composting was considerably high with OEF above 1000 $OU_E\ g^{-1}OM_0$. Emissions from SS and MSW composting are commonly canalized and abated by end-of-pipe technologies. Contrarily, TM and SPS were collected in farms where they are composted in windrows at open air in the absence of odor control systems. Because of the financial limitations to invest on odor abatement technologies in such a rural context, the improvement of composting operational conditions (i.e., turning frequency, bulking agent addition, co-composting, and pile moisture) could represent the best cost-effective strategy to diminish the odor and chemical impact of emission from on-farm composting (Supplementary material, section 1S).

Most of the literature on OEF is addressed toward the estimation of odors in WWTP (Capelli et al., 2009), swim housing (Schauberger et al., 2013) and landfills (Lucernoni et al., 2016). However, OEF inventories for anaerobic digestion and composting process are scarce. Sironi et al. (2006) conducted a first OEF assessment at different operational stages of 40 composting units. This study revealed that the aerobic treatment of MSW is the largest odor source in composting facilities, exhibiting a mean OEF of $1.4 \cdot 10^5\ OU_E\ kg^{-1}$(fresh weight). Despite the difference on treatment scale, this reference value agreed with the OEF obtained for MSW composting in our pilot study ($4.6 \cdot 10^5\ OU_E\ kg^{-1}$ FW). OEF constitutes an important odor assessment tool used to design better odor control strategies and treatment facilities, as well as input data for odor dispersion and prediction models (Lucernoni et al., 2016). Although our study

provides a complete compilation of OEF for composting of several substrates, further efforts are required for enlarging this OEF dataset under different operational composting conditions and scales.

Co-composting of MSW with green wastes (MSG) had an OEF 21 times inferior to MSW composting (Fig. 3). Co-composting of substrates with different biological stabilities (i.e., digestates and agricultural wastes) should be further investigated as a mean to reinforce odor management in waste treatment units.

3.2. Chemical identification of gas emissions

A total of 60 compounds, belonging to nine chemical categories, were identified during the composting process of 15 substrates (Table 4). Sulfide compounds, terpenes, ketones, and alcohols accounted for 66.7% of the screened compounds. Alkenes, nitrogen compounds, aromatics hydrocarbons, acids, and esters were also determined. Benzene, toluene, and methyl thiocyanate were only detected in the gas samples collected from SPS, TM and ADB composting. The presence of these xenobiotic compounds in agricultural wastes can be linked to the substrates contact with solvents, gasoline and fungicides at the farms drop off areas (Fang et al., 2013).

In contrast to our study, toluene, benzene, ethyl-benzene and, xylene (BTEX) have been widely reported in gas emissions from MSW (Komilis et al., 2004; Scaglia et al., 2011), sewage sludge (Y. Li Zhu et al., 2016) and FW (Mao et al., 2006; Tsai et al., 2008) composting. Emissions of these aromatic compounds are associated with feedstocks containing plastics, solvents (rubbers) and vehicle emissions deposition (Scaglia et al., 2011; Staley et al., 2006). Therefore, some factors could have interfered with the detection of BTEX during composting of these organic matrices. For instance, the interaction of aromatics compounds with organic matter and humic complexes may have led to their sequestration (Eitzer, 1995; Semple et al., 2001), thus hindering their volatilization and stripping to levels no possibly detected by the employed instrumental methods. Despite their hydrophobic character, a fraction of the BTEX compounds could have also been adsorbed onto the organic matrices and wood chips used as a bulking agent. Staley et al. (2006) documented the reduction of toluene emissions due to its interaction with vegetative matter. Xenobiotic–degrading microorganisms likely established into the composting pile could similarly contribute to the abatement of these molecules all along the aerobic treatment (Semple et al., 2001).

Table 4. Identified volatile compounds during the composting process of solid wastes and digestates

Family	Chemical compound	CAS number	Mass to charge ratio (m/z)	Calibration coefficient[a]	LOD (ng)[c]	LOQ (ng)[c]	Henry's constants (mol m^{-3} Pa^{-1})[d]	ODT (mg m^{-3})[e]
Acids	Acetic acid	64-19-7	60	149	0.2-3.6	0.6-10.8	40	**0.019**
	Propionic acid	79-09-4	74	1000	-	-	15	0.017
Alcohols	Methanol	67-56-1	31	950	1.5-2	4.5-6	2	43
	2-Butanol	78-92-2	45	2320	0.1-1.2	0.3-3.6	1.1	0.66
	2-Ethyl hexanol	104-76-7	56	1000	-	-	0.38	0.803[f]
	1-Propanol	71-23-8	31	1000	-	-	1.4	0.24
	Ethanol	64-17-5	31	1942	1	3	1.9	0.99
	2-Methyl-1-propanol	78-83-1	43	1000	-	-	1	0.033
	3-Methyl-1-Butanol	123-51-3	55	686	0.5-6.3	1.5-18.9	0.46	**0.026**
Alkenes	1,3-Pentadiene	504-60-9	67	1000	-	-	0.00014	NF
Aromatic hydrocarbons	Benzene	71-43-2	78	1000	-	-	0.0017	8.7
	Toluene	108-88-3	91	2942	0.07-0.3	0.21-0.9	0.0015	1.24
	Styrene	100-42-5	104	1095	-	-	0.0027	0.15
	p,a-Dimethyl styrene	1195-32-0	132	1000	-	-	NF	1.33[f]
	2-Methyl furan	534-22-5	82	1000	-	-	NF	NF
	Pyridine	110-86-1	79	1000	-	-	1.1	0.2
	2-Pentyl furan	3777-69-3	81	1000	-	-	NF	0.019[f]
	3,5-Dimethyl benzothiophene	1964-45-0	161	1000	-	-	NF	NF
Esters	Ethyl acetate	141-78-6	61	266	-	-	0.059	3.14
	Methyl acetate	79-20-9	43	1000	-	-	0.081	5.1
Ketones and aldehydes	Acetaldehyde	75-07-0	73	1000	-	-	0.13	0.0027
	Acetone	67-64-1	58	469	0.15	0.45	0.27	101
	2-butanone	78-93-3	72	1799	0.1-1.4	0.3-4.2	0.18	1.3
	3-Methyl-2-butanone	563-80-4	86	645	-	-	0.087	1.8
	2-Pentanone	107-87-9	86	640	-	-	0.16	0.098
	3-Methyl-2-pentanone	565-61-7	43	1000	-	-	0.073	0.098
	2-Hexanone	591-78-6	58	1000	-	-	0.15	0.098
	3-Pentanone	96-22-0	86	1000	-	-	0.16	3[f]
	3,3-Dimethyl-2-butanone	75-97-8		1000	-	-	0.045	0.176
	2,3-butanedione	431-03-8	43	887	0.2-7.5	0.6-22.5	0.73	**0.00030**
Nitrogen compounds	Methyl thiocyanate	556-64-9	73	1000	-	-	0.22	NF
	Ammonia	7664-41-7	-	-	-	-	0.59	**1.8**
	Trimethylamine	75-50-3	58	1000	-	-	0.076	**0.00073**
	Acetonitrile	75-05-8	41	1497	0.03	0.09	0.52	22
	Acetonitrile dimethyl amino	926-64-7	83	1000	-	-	NF	-

Table 4. continued

Family	Chemical compound	CAS number	Mass to charge ratio (m/z)	Calibration coefficient[a]	LOD (ng)[c]	LOQ (ng)[c]	Henry's constants (mol m^{-3} Pa^{-1})[d]	ODT (mg m^{-3})[e]
Sulfide compounds	Ethanethiol	75-08-1	-	63274[b]	-	0.006	0.0028	**0.00022**
	Methanethiol	74-93-1	-	59101 [b]	-	0.009	0.0038	**0.00021**
	Hydrogen sulfide	7783-06-4	-	34475[b]	-	0.014	0.001	**0.00047**
	Dimethyl sulfide	75-18-3	-	37376[b]	-	0.024	0.0053	**0.0069**
	Dimethyl disulfide	624-92-0	-	37589[b]	-	0.013	0.0058	**0.0098**
	Sulfur dioxide	7446-09-5	64	1000	-	-	0.013	2.3
	Dimethyl trisulfide	3658-80-8	126	301	-	-	0.021	0.014[f]
	Methyl propyl disulfide	2179-60-4	90	1000	-	-	NF	NF
	Carbon disulfide	75-15-0	72	1000	-	-	0.00061	**0.49**
	Dimethyl sulfoxide	67-68-5	63	1000	-	-	0.098	NF
Terpenes	*p*-cymene	99-87-6	119	1480	6.25	18.75	0.0013	**0.12**
	Alpha-pinene	80-56-8	93	609	1.4-3.1	4.2-9.3	0.00029	**0.22**
	Camphene	79-92-5	93	1000	-	-	0.0001	28[f]
	Beta-pinene	127-91-3	93	475	10.6	31.8	0.00015	***0.28***
	3-Carene	13466-78-9	93	651	0.4-3.7	1.2-11.1	0.00016	9.3[f]
	Myrcene	123-35-3	93	1000	-	0	0.00087	0.14[f]
	Limonene	5989-27-5	68	227	4.4-10.7	13.2-32.1	0.00026	**0.18**
	Fenchone	1195-79-5	81	1000	-	-	NF	2.3[f]
	Camphor	76-22-2	95	1000	-	-	0.12	2.84[f]
	Eucalyptol	470-82-6	154	1000	-	-	0.059	0.0051[f]
	Isoterpinolene	586-63-0	121	1000	-	-	NF	NF
	Beta-terpinene	99-84-3	93	1000	-	-	NF	NF
	Gamma-terpinene	99-85-4	93	1000	-	-	0.00038	55[f]
	(-)-Thujone	546-80-5	81	1000	-	-	NF	27[f]
	Thymol	89-83-8	135	1000	-	-	3	0.05[f]

[a] Mean calibration coefficients for five experimental campaigns.
[b] Mean calibration coefficient responses for GC coupled to electrochemical detection (MEDOR).
[c] LOD: Limit of detection; LOQ: Limit of quantification.
[d] Henry's constants as reported in Sander (2015), NF: not found.
[e]Odor detection thresholds (ODT) measured by dynamic olfactometry are in bold. ODT reported by Nagata (2003) are underlined
[f]ODT documented in Van Gemert (2011) compilation.

3.3. Volatile compounds quantification

The identified chemical families contributed to a different extent to the overall cumulative mass of volatile compounds as depicted in Fig. 4. Despite the high complexity and variability involving VOC, ammonia and VSC production in composting, the type of substances detected at the exhaust gas air was directly associated with the nature of the substrates composted. For instance, substrates with a reduced content of vegetal materials, such as agricultural wastes and sewage sludge, showed low terpenes production, varying from 0.07 up to 21% of the total mass emissions (Fig. 4). Besides vegetal feedstock, wood chips can also constitute an essential source for terpenes generation (Maulini-Duran et al., 2013a). Therefore, terpenes emissions in sewage sludge treatment were probably produced by the significant content of the bulking agent (Table 2) in the compostable mixture. In contrast, terpenes exhibited considerably high PC_i (21-90%) along the composting process of biowastes, OFMSW, and green wastes. These organic matrices were mainly constituted of fruits, vegetables, leaves, brush, and food waste. Hence, the high terpene emissions for substrates with lignocellulosic content were likely derived from the decaying process of vegetable material and bacterial degradation of lignin and cellulose (Eitzer, 1995).

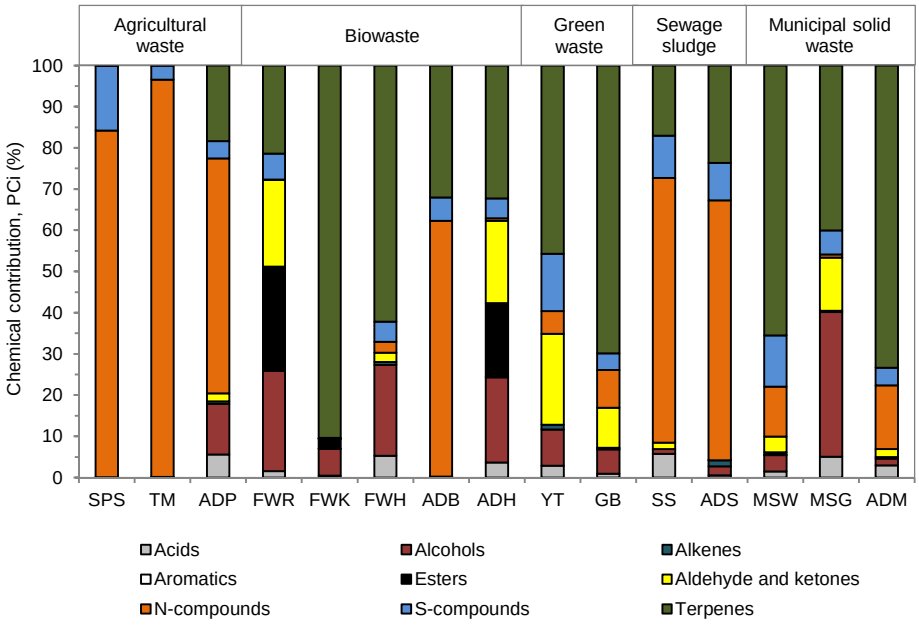


Fig. 4. Chemical contribution PC_i (%) of identified chemical families during the composting process of solid wastes and digestates

The cumulative mass emissions for the identified volatile compounds are summarized in Supplementary material (Table 2S). The highest volatile compounds emissions were observed upon aerobic treatment of raw organic matrices such as food waste (FWR and FWK), turkey manure (TM) and sewage sludge (SS) with cumulative mass emissions ranging from 4385 up to 28395 mg $kg^{-1}OM_0$. The major chemical contributors emitted are shown in Fig. 5. Raw substrates were plotted separately from

digestates to evaluate their emissions profiles better. Because of their similar compositions, emissions from sewage sludge and agricultural waste were gathered in Fig. 5A.

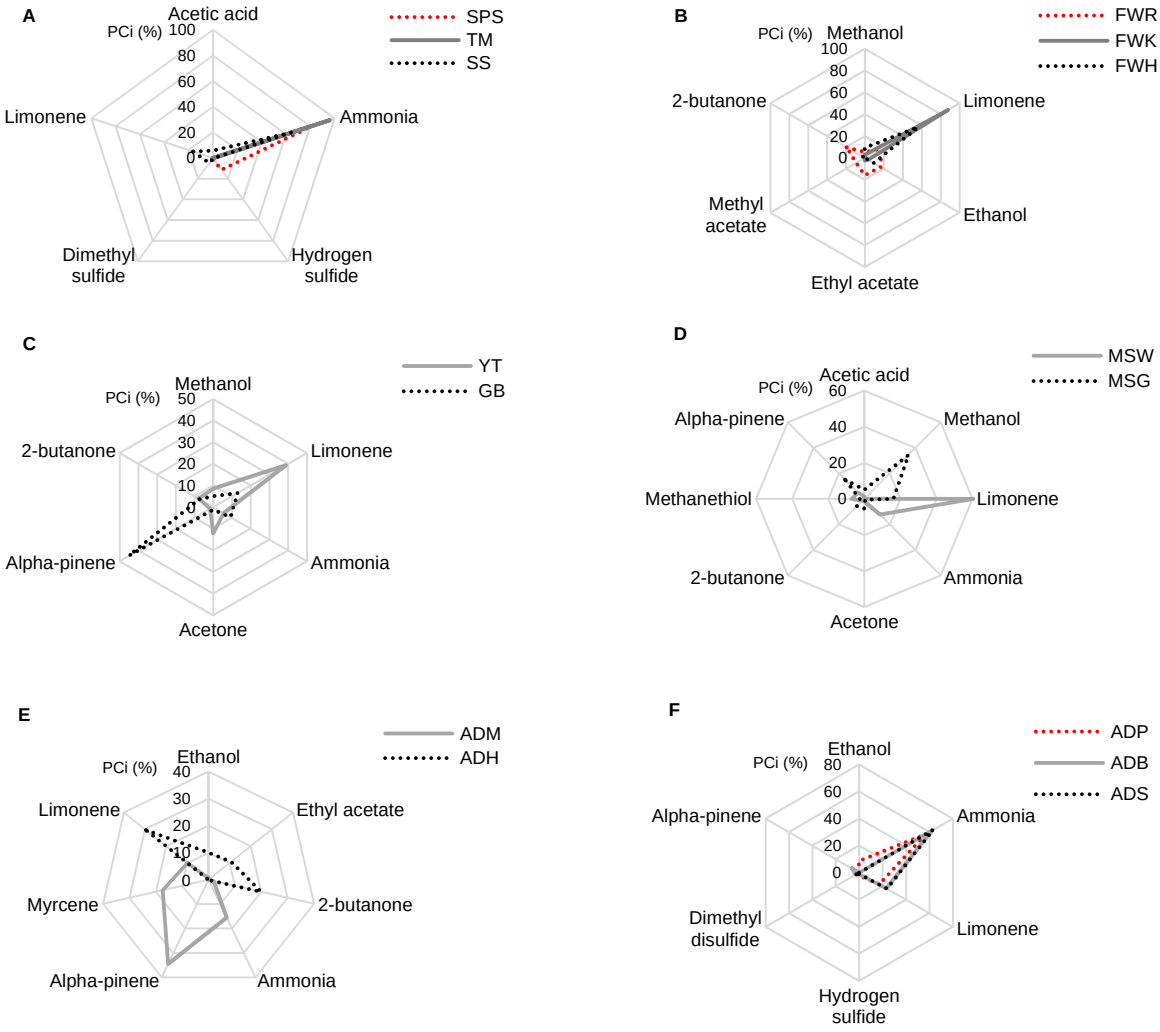


Fig. 5. Chemical contribution PCi (%) of major volatile compounds emitted upon composting of agricultural waste and sewage sludge (**A**), biowaste (**B**), green waste (**C**), municipal solid waste (**D**), and digestates (**E**, **F**)

Emissions of sulfide compounds occurred with low PC_i for all substrates (Fig. 4), except for SPS aerobic treatment. Considering that S-containing species are produced via anaerobic degradation of proteins and sulfates (Higgins et al., 2006; Rosenfeld et al., 2007), the presence of anaerobic pockets was expected to occur within the composting matrix. Even under forced aeration conditions, anoxic and anaerobic zones could be present because of three principal reasons: i) oxygen depletion due to high oxygen consumption rates when degrading organic matter at the first stage (thermophilic phase) of composting process (Maulini-Duran et al., 2013a) ii) formation of preferential pathways that prevent biofilms into the composting bed from being supplied with oxygen, and iii) low porosity of substrates

which hinders oxygen passage and diffusion through biofilms. Hence, H_2S had a PC_i of 11.4% in SPS experiment (Fig. 5A) probably due to the limited aeration supply and the lack of bulking agent.

3.3.1. Agricultural wastes

Emissions from agricultural wastes were mainly composed of nitrogen compounds with PC_i varying from 84% to 96.4% (Fig. 4). For TM and SPS, ammonia was the most abundant compound emitted representing from 83.4% to 95.8% of the total emission (Fig. 5A). As a result of urine hydrolysis and proteins degradation (Webb, 2001), animal manures contain significant amounts of NH_3/NH_4^+ that can be readily volatilized and lost under forced aeration treatment. Similarly, de Guardia et al. (2010b) determined strong ammonia emissions (1000-1700 mg $kg^{-1}OM_0$) during composting treatment of SPS. Trimethylamine (TMA) was only detected in composting gas samples from TM and SPS. This observation can be related to animal production systems, which produce large amounts of feces and urine resulting in significant emissions of TMA in the atmosphere (Sintermann et al., 2014).

3.3.2. Biowastes

In general, composting emissions from FW were dominated by terpenes, ketones, esters, and alcohols (Fig. 4). These VOC have been identified in household FW (Mao et al., 2006; Tsai et al., 2008) and biowaste (Schlegelmilch et al., 2005). In contrast to our finding, Komilis et al. (2004) concluded that sulfide compounds were the primary chemical contributor along the aerobic treatment of FW (Komilis et al., 2004). The difference among published data could be linked to the high impact of process conditions (aerobic or anaerobic) and waste characteristics.

When comparing the FW emission profiles among them, different emission trends were observed based on the origins and composition of substrates. FWK, consisting of vegetable, fruits, and peels, had the most concentrated terpenes emissions with a PC_i of 88%. On the other hand, FWR and FWH, containing not only vegetable material but also meat, cooked food, and others (Table 1), presented more substantial contributions of ethanol, methanol, ethyl acetate, methyl acetate and 2-butanone (Fig. 5B). These oxygenated compounds are primarily produced by the partial aerobic degradation of organic matter during biological treatment (Gallego et al., 2012; Shao et al., 2014).

3.3.3. Green wastes

Vegetable-derived compounds such as terpenes, ketones, and alcohols were extensively produced when composting YT and GW (Fig. 4). Defoer et al. (2002) reported those chemical groups as significant contributors at the exhaust air from composting plants treating vegetable fruits and garden wastes. In this

study, limonene and alpha-pinene were the most emitted substances with chemical contributions of 39% and 45%, respectively. Likewise, acetone and 2-butanone were actively emitted. Methanol, an intermediary product of microbial metabolism of wood and plants, was the most relevant alcohol with PC_i varying from 5% to 8% (Fig. 5C).

3.3.4. Sewage sludge

In decreasing order, the most emitted chemical families were nitrogen compounds, terpenes, and sulfide compounds. Ammonia represented 64% of the overall cumulative emission (Fig. 5A). The emission factors obtained upon aerobic treatment of SS (4385 mg $Kg^{-1}MO_0$) agreed with the one published by Maulini-Duran et al. (2013a) at laboratory scale (4456 mg $Kg^{-1}OM_0$). Cumulative mass emissions were comparable between these studies regardless of the difference in experimental scales (lab and pilot-scale). Such comparability highlights the feasibility of up-scaling emission factors as benchmarks for air-pollution control at composting facilities.

Limonene, DMS, CH_3SH, and acetic acid were the main VOC and VSC contributors in composting gas emissions of SS (Fig. 5A). Sulfur-containing compounds and limonene have been previously found in SS composting process as core indicators for odor nuisance (Durme et al., 1992; Y. Li Zhu et al., 2016). The presence of acetic acid could be associated with anoxic conditions and partial anaerobic degradation of organic matter.

3.3.5. Municipal solid waste

The leading chemical groups released during MSW composting were terpenes, nitrogen compounds, sulfide compounds, ketones and alcohols (Fig. 4). In accordance with Scaglia et al. (2011) and Maulini-Duran (2013b), limonene was found to be the main volatile compound emitted upon OFMSW composting, accounting for 60% of the total cumulative mass (Fig. 5D). Furthermore, nitrogen compounds content in exhaust gas was entirely constituted by ammonia, placed as the second most emitted substance with a cumulative emission of 213 mg $Kg^{-1}OM_0$. This ammonia emission factor was close to values measured at lab-scale (Pagans et al., 2006a) but far from the one (14286 mg $kg^{-1}OM_0$) measured in a real-scale plant (Cadena et al., 2009). The main sulfur compound was methanethiol, representing from 7.2% to 2.2% of total emission for MSW.

Particular variations were observed when OFMSW was composted with green wastes. MSG emitted alcohols and ketones actively with PC_i of 35% and 13%, respectively (Fig 4). Hence, methanol was the leading volatile compound, followed by limonene and alpha-pinene (Fig. 5C). The high content of lignocellulosic material in the composting process could be linked not only to terpenes generation but also oxygenated compounds production (Defoer et al., 2002).

3.3.6. Anaerobically digested substrates

The total cumulative emissions of digested were two up to 70 times inferior to those observed when composting raw substrates (Supplementary material, Table 2S). Compared to raw organic matrices, digestates typically contain lower amounts of readily biodegradable organic matter (Tambone et al., 2010). Less access to nutrient sources probably led to a decline in microbial activity upon aerobic post-treatments of digestates and consequently a reduction in volatile compounds production.

For ADP, ADB, and ADS, ammonia emissions were dominant with PC_i of 57%, 62%, and 63%, respectively (Fig. 5F). This tendency can be linked to the low C/N ratios of these substrates (Supplementary material, Table 1S). During anaerobic digestion, organic matter is turned into CO_2 and CH_4, and organic N is mainly hydrolyzed and embedded into the organic matrices as simpler N-containing compounds and NH_3/NH_4^+ (Rosenfeld and Suffet, 2004). The NH_3 emission factor obtained for ADS treatment agrees with the value measured by Pagans et al. (2006a) of 1160 mg $Kg^{-1}OM_0$ but differs significantly from the cumulative emission (40 g $Kg^{-1}OM_0$) reported by Zhen et al. (2012). The substrates nature, process conditions, and possible ammonia absorption onto bulking agent could cause such as variability among studies (Zeng et al., 2012).

Unlike the other digestates, ADH and ADM presented low NH_3 PC_i of 0.1% and 15%, respectively (Fig. 5E). Some possible facts could explain this trend: i) ADH was a raw digestate treated during 20 days at the methanization plant, meaning that was partially stabilized as proved by its high C/N ratio (Supplementary material, Table 1S) ii) ADM was a mixture of anaerobically digested OFMSW with lignocellulosic material which increased considerably its ratio C/N and possibly minimized its NH_3 emission potential.

During digestates composting, the most emitted VOC were terpenes which represented from 18% up to 73% of the total cumulative emissions. Limonene (PC_i= 10-31%), alpha-pinene (PC_i= 0.6-34%) and myrcene (PC_i= 7.4% for ADM) were the principal terpenes detected (Fig. 5E and Fig. 5F). Terpenes emission were prompted by the presence of wood chips used as a bulking agent, but also as a result of the partial degradation of organic matter derived from vegetative material (Maulini-Duran et al., 2014; E Pagans et al., 2006b). Except for ADS, digestates were obtained through anaerobic digestion of vegetable feedstocks containing fruits, yard trimmings, vegetables, and trees branches, commonly associated with terpenes content (Staley et al., 2006b). Furthermore, Orzi et al. (2010) demonstrated that terpenes are degraded in a minor extent along the anaerobic treatment of MSW. Hence, terpenes not degraded upon anaerobic digestion were likely stripped and volatilized once the forced aeration was set up, resulting in significant emission rates along the digestate post-treatment. Limonene and alpha-pinene were previously identified in VOC emissions from the aerobic treatment of ADS at the laboratory scale (Maulini-Duran et

al., 2013a) and real scale (Durme et al., 1992). Sulfide compounds also occurred upon digestates composting (Fig. 4), with relative low chemical contribution rates no superior to 4.5%.

3.4. Characterization of major odor contributors

3.4.1. Odor detection thresholds (ODT)

ODT can vary largely from some order of magnitudes in reported ODT datasets (Parker et al., 2012). To reduce the impact of ODT variability in OAV calculations, 15 ODT were determined following EN 13725 guidelines. As seen in Table 4, tested substances included some of the most frequently detected compounds and known odorants such as VSC, trimethylamine, and 2,3-butanedione. The effect of panelist selection criteria on ODT determination was lowered by repeatedly screening the panelist's group with n-butanol. A panelist average detection threshold of 148 ± 84 μg m^{-3} for n-butanol was obtained during the olfactometric measurements. The results of this calibration process successfully fulfilled the EN 13725 requirements (62-246 μg m^{-3}).

Wu et al. (2017) measured 51 ODT by dynamic olfactometry, obtaining ODT values 15 times higher than those calculated by the triangle bag method in Nagata's report. ODT measured in this study were on average three times larger than the ones measured by Nagata (2003). Moreover, median relative deviations (RD) of 37% and 71% were attained when comparing measured ODT with values reported by Nagata (2003) and Wu et al. (2017), respectively (Supplementary material, Table 3S). As explained by Ueno et al. (2009) and Wu et al. (2017), discrepancies on ODT obtained among studies could be caused by differences on panel selection criteria, type of dilution presentation and variations on Z_{50} calculation. For example, the geometric mean of Z_{50} in dynamic olfactometry is evaluated in an ascending concentration order, whereas the triangle bag method assessed Z_{50} in descending series. In accordance with our study, Ueno et al. (2009) demonstrated that ODT of 5 compounds evaluated by dynamic olfactometry were three times larger than values yielded by the triangle bag method.

ODT from Nagata's report were preferably adopted to compute OAV for those compounds not tested by dynamic olfactometry. However, 13 ODT were not determined by Nagata (2003) and then consulted in Van Gemert (2011) compilation (Table 4). ODT for 7 compounds were not found in the literature, a fact limiting this odor assessment approach because of possible odor underestimation (Gallego et al., 2012). Hence, further ODT measurements must be conducted by well-trained odor panels and standardized methodologies (EN 13725) to strengthen the odor monitoring and reliability of studies involving OAV calculation (Schiavon et al., 2017). Enlarging ODT datasets is essential to validate the reproducibility of ODT measurement among different laboratories and support the establishment of a unified ODT dataset for odor assessment (Wu et al., 2017).

3.4.2. Odor contribution

The odor contribution of the identified chemical groups and substances was assessed by weighting OAV_{max} with $SOAV_{max}$ (Fig. 6A and Fig. 6B). The highest OAV_{max} represented an upper bound or the worst case scenario when monitoring odorants along the composting campaigns. Hence, OAV_{max} allowed determining the major odor contributors upon aerobic treatment. Supplementary material (Table 4S) provides OAV_{max} used to develop this methodology. The possible synergetic and antagonist interactions occurring among odorants were beyond the scope of this monitoring strategy.

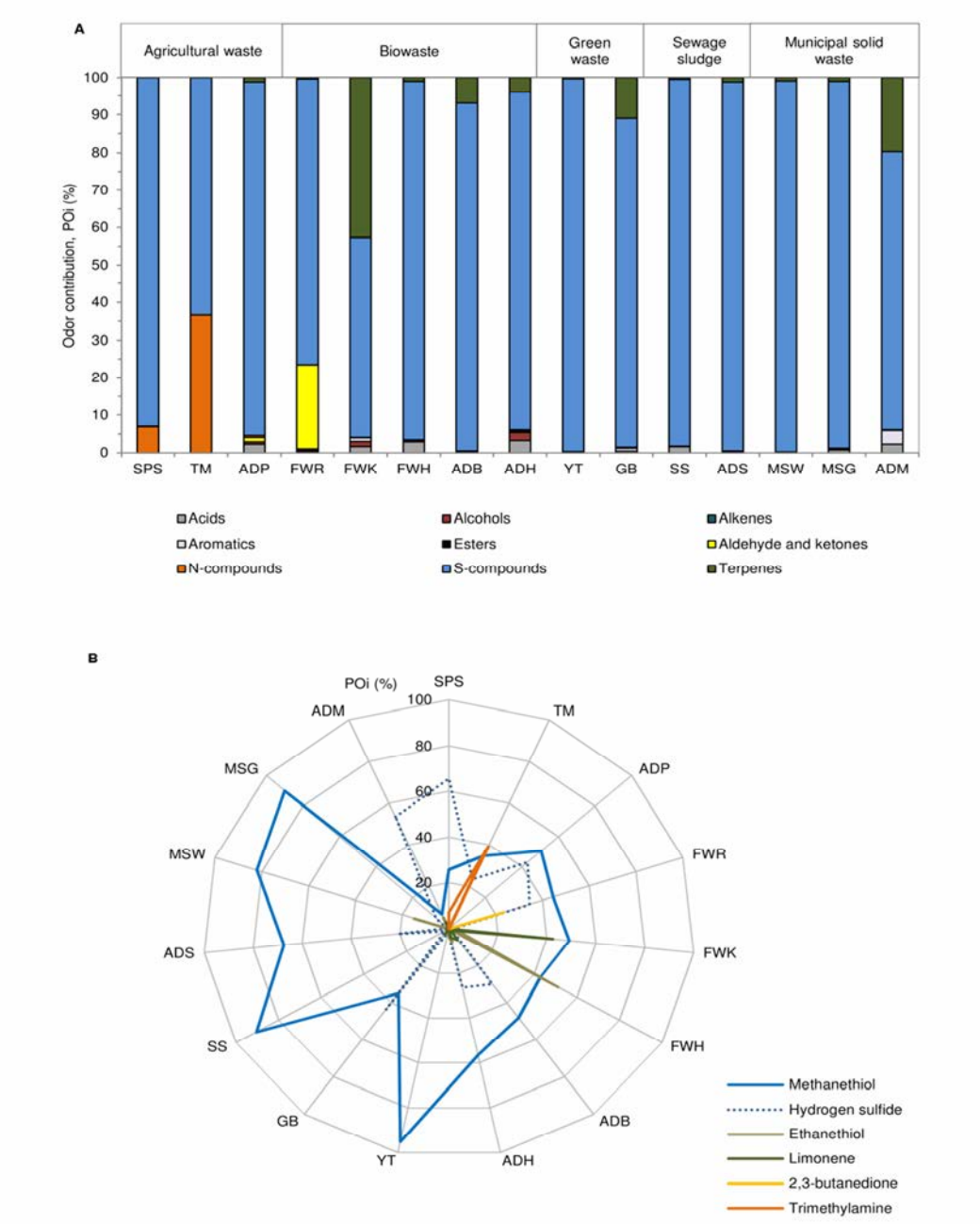


Fig. 6. Odor contribution (PO_i, %) of identified chemical families (**A**) and main odorants (**B**) emitted upon the composting process of solid wastes and digestates

Volatile sulfur compounds were the major odor contributors (PO_i= 54-99%) for all composted substrates (Fig. 6A). The odorous activity of these substances is associated with their high volatility, low ODT and thus significant potential to create odor sensory stimulus even at reduced concentrations (Table 4). The main VSC contributing to odors were CH_3SH, ethanethiol, and H_2S as they represented from 34% up to 95% of the total $SOAV_{max}$ (Fig. 6B). Methanethiol was commonly targeted as the main odorant for 73% of the composting experiments. H_2S was the main odor contributor for SPS, ADM and GB treatment, whereas ethanethiol exhibited the largest OAV_{max} upon FWH composting. Likewise, some studies have demonstrated the crucial relevance of S-containing compounds on odor nuisance generation along composting of sludge from pig slaughterhouse sludge (Blazy et al., 2014a), OFMSW (Scaglia et al., 2011; Shao et al., 2014), FW (Tsai et al., 2008), SS and ADS (Maulini-Duran et al., 2013a; F. Zhu et al., 2016). Because of their importance on odor management at waste treatment units, VSC abatement technologies and reduction strategies are addressed in Supplementary material (section 1S).

The OAV profiles of CH_3SH for all treated substrates are given in Fig. 7. A log transformation of OAV was used to limit variance from the input odor data whereas the substrate composted. Such data normalization enabled to illustrate emissions patterns of this odorous compound through the biological process. CH_3SH peak odor emissions occurred upon 2-7 days of the process for 87% of the compostable substrates. Once reached the odor peak values, CH_3SH odor potential tended to drop off or disappear at the final stage (20-30 days) of the aerobic treatment when biological activity typically slows down. CH_3SH was generally emitted during the first days of the composting process when high amounts of oxygen are up-taken to degrade readily organic matter. Because of oxygen depletion, oxygen transfer through biofilms is minimized, and thus anaerobic sites may be formed within the composting matrix (Higgins et al., 2006; Zhang et al., 2013). Additionally, the high temperatures typically found at the first stage of the aerobic process could have increased the gaseous transfer rates of VSC through the biofilms. Early VSC emissions were also identified during composting of MSW (Zhang et al., 2013) and mushrooms (Noble et al., 2001).

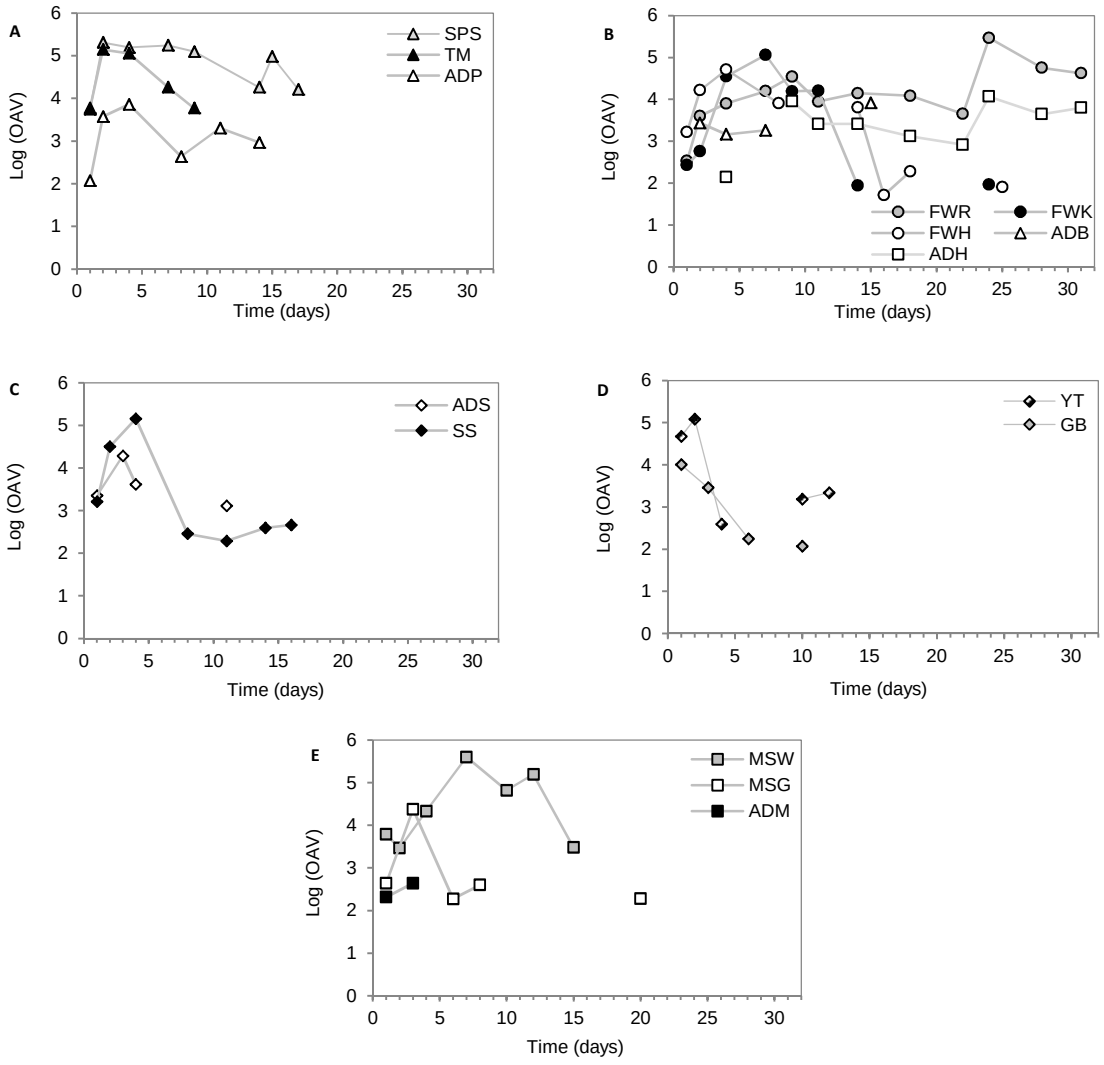


Fig. 7. OAV profiles for CH_3SH upon composting process of agricultural wastes (**A**), biowastes (**B**), green wastes (**C**), sewage sludge (**D**), and municipal solid waste (**E**)

In addition to VSC, other chemicals families, namely N-containing compounds, ketones, and terpenes also contributed moderately to $SOAV_{max}$ (Fig. 6A). For SPS and TM, odor contribution from nitrogen compounds was led by TMA which exhibited PO_i of 7% and 39%, respectively (Fig. 6A). TMA, a fishy odor molecule, was also determined as crucial odor contributor in previous studies on FW (Tsai et al., 2008) and OFMSW (Scaglia et al., 2011) composting. FWK gas samples had extremely high concentrations of limonene which were reflected on its PO_i of 42.5%. Concerning ketones, 2,3-butanedione (PO_i= 23.4%) was identified as a potential odor source from FWR aerobic treatment (Fig. 6B). This butter-like odor compound, commonly used as an additive in the food industry, was the leading cause of odor pollution in Llobregat River (Spain) (Díaz et al., 2004); Yet, no previous reports of this molecule were found in gas emissions from waste treatments.

4. Conclusions

The chemical composition of gas emission from composting varied considerably depending on the substrates nature and operational conditions. In general, terpenes and oxygenated compounds (alcohols, esters, and ketones) contributed substantially to the total mass emissions of organic matrices containing vegetable and food feedstock such as biowastes, municipal solid waste and green wastes. In contrast, emissions from agricultural wastes, sewage sludge, and some digestates were mainly composed of ammonia.

The strong odor impact of emission generated upon composting of raw substrates such as agricultural waste and food waste was proved by their odor emission factors (OEF) superior to 1000 OU_E $g^{-1}OM_0$. Compared to solid wastes composting, the aerobic treatment of digestates exhibited lower cumulative mass emissions of compounds and OEF below to 30.5 OU_E $g^{-1}OM_0$. Such difference was associated with the higher stabilization degree of organic matter present in anaerobically digested substrates.

Although VSC had relatively low chemical contributions (PC_i= 0.2-15%), their odorous potential was highlighted by the proposed OAV methodology. Methanethiol, ethanethiol, and hydrogen sulfide were the leading odorants for all composting experiments regardless of the experimental conditions and substrates nature. Odor mitigation strategies could be better implemented and designed by taking into account these identified odorous compounds. Reducing the number of target compounds can enhance the efficiency and reduce the costs of odor monitoring programs.

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Supplementary material

Section 1S. Technologies and operational strategies to abate and reduce volatile sulfur compounds (VSC) emissions in composting

VSC reduction and removal from emissions released upon composting operations is currently a hot research topic because of the social implications and increased public concern about odors. Enhancing operational composting conditions constitutes the most straightforward and cost-effective approach to reduce VSC emissions during composting of solid wastes and digestates. Instinctually, the control of critical parameters governing the aerobic treatment process such as humidity, level of aeration and porosity can lead to obtain more stabilized organic substrates and limit the occurrence of anaerobic zones commonly linked to the production of odorous intermediaries from anaerobic metabolism such as VSC (Wei et al., 2017; Zang et al., 2016).

A first key composting practice used to tackle VSC emissions is the addition of bulking agents such as wood chips, cornstalk, and rice straw to improve the air-free space and airflow distribution into the composting pile (Zeng et al., 2016), as well as a strategy to regulate nutrients content and C/N ratio (Wei et al., 2017). Zhang et al. (2013) reported that composting food waste with cornstalks at a mixing ratio of 4:1 (wet weight) could significantly diminish VSC emission in 67 %. In accordance with this study, Shao et al. (2014) observed that VSC cumulative mass emissions upon OFMSW composting were reduced from 40 to 28 mg kg^{-1} (dry weight) through the use of incorporation rates of rice straw ranging from 10 to 30 (% volume to volume), respectively.

Similarly, the aeration rate and oxygen supply are critical operational parameters influencing VSC emissions. He et al. (2018) demonstrated that high degrees of organic matter stabilization and oxygen levels lowered the emission rates and cumulative mass of carbonyl sulfide, carbon disulfide, and methanethiol along sewage sludge composting. These authors recommended controlling air inflows because dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) could be emitted through excessive aeration. The principal reason why DMS and DMDS are released when applying high aerations rates is that they are produced by oxidative abiotic reactions. Zhang et al. (2016) determined that using aeration rate of 0.2 L min^{-1} kg^{-1}(dry weight) could reduce the emission of VSC and NH_3 along kitchen waste composting. Likewise, Blazy et al. (2014) documented a downward trend of H_2S emissions in factor 5 to 10 throughout the aerobic treatment of pig slaughterhouse sludge with regulated aeration flows (1.7-4 L h^{-1} kg^{-1} sludge) that were high enough to warrant aerobic decomposition of organic matter, but not excessive to limit stripping phenomena (Blazy et al., 2014).

Although operational composting conditions can significantly reduce VSC emissions, the occurrence of this type of substances during aerobic degradation is almost unavoidable because of the presence of

anaerobic microsites, bed channeling phenomena and oxygen depletion during the thermophilic stage of composting (Scaglia et al., 2011; Smet and Van Langenhove, 1998). Odor detection thresholds (ODT) for VSC are considerably low (Table 3S). As a result, these molecules can produce odor nuisances even at extremely low concentrations and drive to neighboring odor complaints. For this reason, waste treatment units are typically equipped with end-of-the-pipe technologies that warrant the full abatement or drastic reduction of VSC and other odorous substances to levels not detectable by the surrounded communities. These abatement technologies are principally divided into conventional treatments (physicochemical methods) and bio-treatments conducted through bioreactors set in multiple configurations (Giri et al., 2014). The selection of the most suitable technology depends on multiple factors including the financial investment capacity of the waste treatment plants, type of VSC to be treated, and the concentration range of the emitted substances (Busca and Pistarino, 2003).

Some of the conventional methods more widely developed to abate VSC in gas streams are wet scrubbing, adsorption onto activated carbon, thermal and catalytic combustion, and chemical /UV oxidation (Busca and Pistarino, 2003; Giri et al., 2014; Wei et al., 2017). Among these physicochemical methods, wet scrubbing and adsorption onto activated carbon are perhaps the treatment technologies more employed in waste treatment units and WWTP because of their significant VSC removal efficiencies and relatively low cost per unit (Charron et al., 2006; Giri et al., 2014; Jana and Sarkar, 2018; Smet and Van Langenhove, 1998). Despite their great abatement capacities, these removal processes required a continuous regeneration of the solid and liquid phases that serve as adsorbents. In the case of wet scrubbing, another clear drawback is the generation of sulfate-containing solutions and hazardous byproducts such as chlorinated compounds (Busca and Pistarino, 2003; Charron et al., 2006; Giri et al., 2014).

In contrast to the physicochemical methods, bio-treatments are based on the capacity of microbial consortiums to degrade and transform dangerous air pollutants into CO_2, energy, microbial mass and less hazardous compounds (Hort et al., 2009). Mainly, biofiltration is the principal bio-treatment consisting on the transfer of gaseous compounds to a bio-filter media (i.e., mature compost, peat, wood chips, wood bark, etc.) where they are adsorbed and mineralized (Wei et al., 2017). Other important bio-reactors used for VSC and odorous removal are biotrickling filters, bioscrubbers, and membrane bioreactor (Giri et al., 2014). However, it is well-known that biofiltration is the preferred abatement technology in composting units and other waste treatment units because of their cost-effectiveness, simple operation, and significant removal efficiency of VSC and other VOC (Giri et al., 2014; Wei et al., 2017). For instance, biofilters are operated at ambient temperatures (15-30 °C) without producing toxic by-products. Concerning VSC abatement, Giri et al. (2014) reported removal efficiencies of up to 90% of DMS through bofiltration. Similarly, Hort et al. (2009) attained 100% removal of ethanethiol, DMS, and DMDS while treating exhaust gases from composting with a biofilter composed of sewage sludge and yard waste compost.

Table 1S. Physicochemical characteristics of composted organic substrates

Substrates		Moisture (%)	OM (% DM)	Total carbon (gC kg^{-1} DM)	TKN (gN-K kg^{-1} DM)	Ratio C/N	COD (gO_2 kg^{-1} DM)	NH_4^+/NH_3 (gN-NH_4^+ kg^{-1}DM)	Total sulfur (gS kg^{-1} DM)
Agricultural waste	SPS	68.53	72.50	385.38	39.40	9.78	1086.62	14.52	6.01
	TM	68.75	80.50	406.79	50.88	8.00	1081.00	19.52	7.84
	ADP	62.50	64.57	323.17	35.90	9.00	881.14	10.89	6.58
Biowaste	FWR	72.66	94.79	523.56	33.03	15.85	1676.00	0.64	1.94
	FWK	80.43	93.71	508.30	32.53	15.63	1571.44	0.14	1.72
	FWH	69.44	92.81	474.71	20.79	22.83	1321.97	0.35	1.77
	ADB	76.53	81.23	441.12	43.46	10.15	1308.00	19.60	6.74
	ADH	59.71	61.23	336.87	15.88	21.21	1225.16	4.79	2.00
Green waste	YT	80.82	85.70	433.03	22.39	19.34	1228.29	0.40	3.15
	GB	53.66	57.37	318.16	14.55	21.87	855.20	1.41	1.61
Sewage sludge	SS	84.89	76.84	415.90	85.02	4.89	1183.23	7.74	8.10
	ADS	83.87	65.20	363.26	69.56	5.22	1131.07	11.85	11.96
Municipal solid waste	MSW	56.24	75.10	391.54	17.97	21.79	1069.92	3.50	2.13
	MSG	55.19	71.98	375.62	15.21	24.70	1001.09	3.09	2.66
	ADG	70.13	56.37	323.61	20.98	15.42	808.34	7.72	2.66

OM: Organic matter content; DM: Dry matter; TKN: Total Kjeldahl Nitrogen; COD: Chemical oxygen demand.

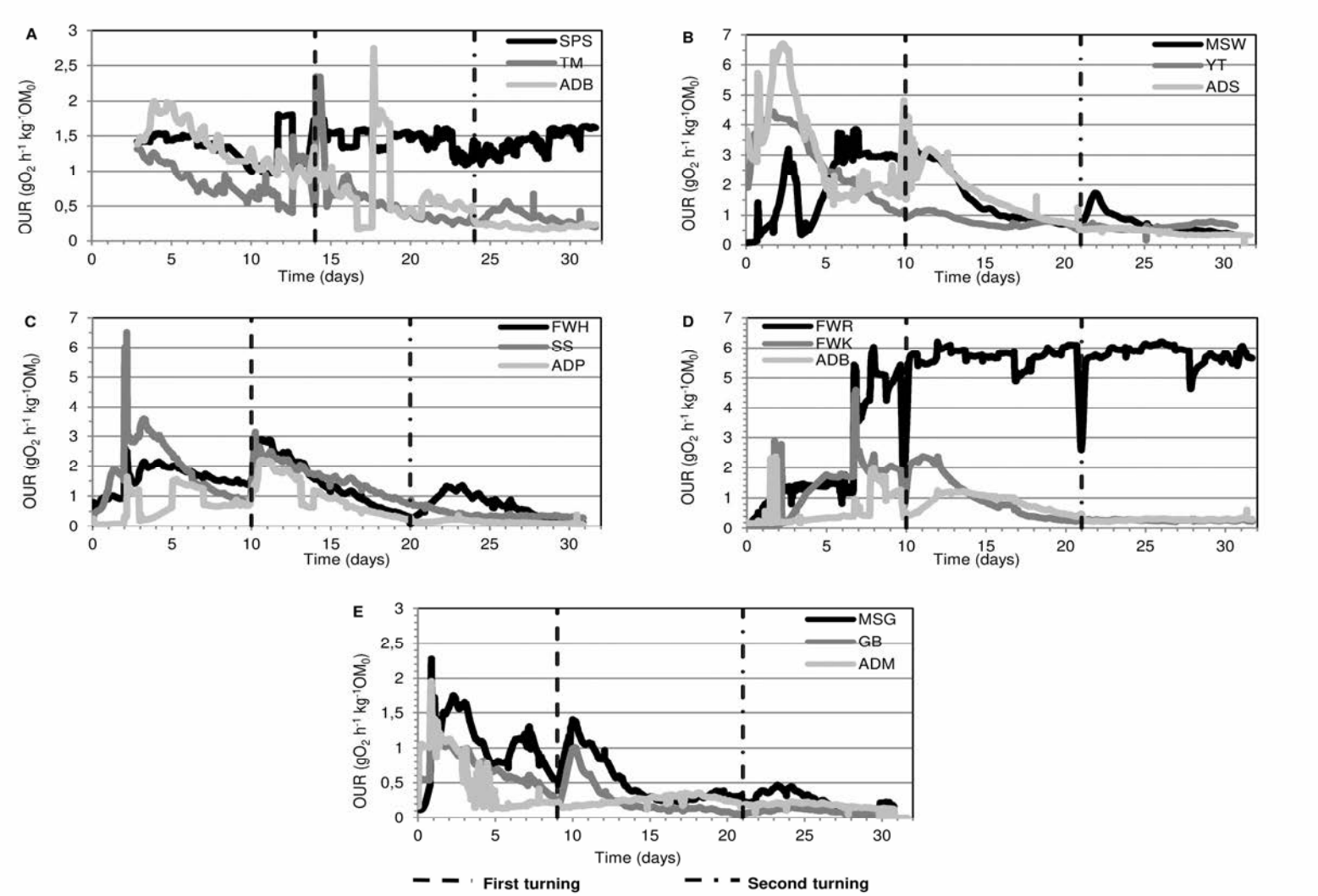


Fig. 1S. Oxygen uptake rates (OUR in $gO_2\ h^{-1}\ kg^{-1}OM_0$) profiles along composting of solid wastes and digestates

Table 2S. Odor emission factors (OEF) and cumulative mass emissions of volatile compounds identified during composting of solid wastes and digestates

	Cumulative mass emission (mg compound kg^{-1} OM_0)													
Waste category	**Agricultural waste**			**Biowaste**					**Green waste**		**Sewage sludge**		**Municipal solid waste**	
Chemical compound	**SPS**	**TM**	**ADP**	**FWR**	**FWK**	**FWH**	**ADB**	**ADH**	**YT**	**GB**	**SS**	**ADS**	**MSW**	**MSG**	**ADM**
Acetic acid	0.10	0.13	20.88	193.70	123.88	50.97	0.65	19.55	7.06	6.85	251.88	5.56	26.36	12.84	6.72
Propanoic acid			0.17											0.035	
Methanol	0.17	0.84	8.41	670.84	789.93	90.14	0.067	29.24	20.88	36.20	36.12	23.67		88.92	2.09
2-Butanol	0.021	0.035	4.89		0.36		0.0039	17.32	0.78		13.69		3.77		
2-Ethyl hexanol	0.64	0.15					0.12								
1-Propanol													0.57		
Ethanol			32.27	2083.86	939.96	87.95		54.36		6.25			64.13	1.55	1.67
2-Methyl-1-propanol			0.72	84.52	122.02			3.00							
3-Methyl-1-Butanol				192.62		34.03		6.71							
1,3-Pentadiene			2.32			6.64			2.91	0.77		16.32	2.43		
Benzene	0.0088	0.0046					0.024								
Toluene	0.0020	2.44					0.065								
p-cymene				244.84	483.34	4.81		4.55		17.44	11.49			10.84	17.08
Styrene							0.0022								
p,α-Dimethylstyrene				38.69	13.36			1.13		1.54				0.87	0.97
2-Methyl furan		0.029								0.63					
Pyridine		0.18													
2-Pentyl furan	0.012	0.015					0.053								
3,5-Dimethylbenzo[b]thiophene				0.20											
Ethyl acetate				1978.86	655.77			57.57					10.26		
Methyl acetate				1151.96	18.70			37.94							
Acetaldehyde			0.85												
Acetone	1.09	4.88		100.36			0.07		29.93	8.49	39.64		24.72	13.61	
2-butanone	0.53	1.01	6.57	2436.52	4.22	21.89	0.05	107.25	19.46	53.43	28.39		23.54	14.80	4.43
3-Methyl-2-butanone	0.06	0.08					0.00								
2-Pentanone	0.17	0.15					0.01		4.82				16.50	4.72	
3-Methyl-2-pentanone		0.01													
2-Hexanone													1.81		
3-Pentanone										8.56					
3,3-Dimethyl-2-butanone												0.0061			
2,3-butanedione				84.97											
Methyl thiocyanate	0.0020	0.0072													
Ammonia	2888.01	7833.20	214.64	4.39	4.11	25.74	326.20	0.42	13.59	66.57	2814.28	688.63	213.21	2.00	35.57
Trimethylamine	25.36	45.65													
Acetonitrile				6.00				2.96			2.50				
Acetonitrile dimethyl amino	0.31	0.37					0.0016								
Ethanethiol					0.70	15.33		0.12	0.81	0.06			12.22		0.044

Table 2S. Continued

Chemical compound	SPS	TM	ADP	FWR	FWK	FWH	ADB	ADH	YT	GB	SS	ADS	MSW	MSG	ADM
Methanethiol	50.26	16.32	3.11	150.10	46.38	18.79	1.30	3.65	20.75	1.83	108.80	8.56	126.26	6.46	0.12
Hydrogen sulfide	395.95	23.45	8.63	390.59	2.67	3.74	6.83	5.68	3.76	8.26	17.15	10.78	2.87	1.54	4.20
Dimethyl sulfide	38.09	96.06	2.23	4.36	7.91	3.58	4.84	1.13	5.68	11.77	211.92	20.33	59.21	5.60	2.31
Dimethyl disulfide	58.74	142.77	1.75	40.06	8.20	5.46	16.52	1.70	3.25	6.24	39.91	48.61	17.30	1.46	3.07
Sulfur dioxide				161.96							5.29				
Dimethyl trisulfide	0.24	0.62					0.013					10.58			
Methyl propyl disulfide															
Carbon disulfide				36.30				13.54							
Dimethyl sulfoxide										1.01	68.14				
Alpha-pinene	1.57	3.72	3.25	146.08	101.40	44.25	33.74	3.19	4.13	325.76	16.55		85.38	39.08	79.22
Camphene	0.025	0.015					0.74			4.70				0.81	2.93
Beta-pinene	0.43	0.29	1.20	81.88	40.96	7.85	10.62	2.38	10.47	2.93	5.47			0.71	
Carene	0.0019	0.020		97.71	13.56		0.97	4.55	2.57				1.63		
Myrcene		0.016		16.97	101.93	1.92	0.26			21.18				4.79	40.09
Limonene	2.67	1.57	64.90	2087.99	24916.04	540.41	122.06	158.22	95.34	94.15	714.19	257.61	1064.26	41.31	22.96
Fenchone		0.032					0.07								
Camphor		0.021													
Eucalyptol												0.30			
Isoterpinolene										10.23					2.57
Beta-terpinene										5.40					0.08
Gamma-terpinene										21.42				4.05	3.15
(-)-Thujone										2.68				1.33	0.44
Thymol										0.85				0.07	
Total emmision (mg $Kg^{-1}OM_0$)	3464.44	8174.06	376.79	12486.35	28395.40	963.51	525.28	536.12	246.16	725.19	4385.38	1090.95	1756.42	257.41	229.72
Odor emission factor (OEF in $OU_E\ g^{-1}OM_0$)	3089.14	1219.08	20.40	2880.60	253.58	406.47	30.49	27.22	705.55	88.10	1216.79	ND	1406.67	63.63	8.27

ND: Not determined

Table 3S. Odor detection thresholds (ODT) measured by dynamic olfactometry and comparison with values reported by Wu et al. (2017) and Nagata (2003)

Compound	N[a]	Relative losses (%) for storage[b]	Initial conc. (mg m^{-3})[c]	Exposure conc. C_0 (mg m^{-3})[f]	Measured ODT (mg m^{-3})	SD[g]	Reported ODT (Nagata, 2003)	Fold dif.[h]	RD (%)[i]	Reported ODT (Wu et al., 2017)	Fold dif.[h]	RD (%)[i]
Hydrogen sulfide	5	**~0**	1.47-0.37	1.47-0.37	0.00047	0.00029	0.00053	0.89	11.3	0.00042	1.12	11.9
Limonene	3	**~0**	280.7	280.7	0.183	0.041	0.134	1.37	36.6	0.255	0.72	28.2
Acetic acid	3	22.4	104.9	81.40	0.019	0.003	0.016	1.19	18.8	0.88	0.02	97.8
Trimethylamine	3	18.7[c]	1.24	1.01	0.00073	0.00011	0.00006	12.17	1116.7	0.0017	0.43	57.1
Methanethiol	3	**~0**	1.05	1.05	0.00021	0.00007	0.00031	0.68	32.3	-	-	-
Dimethyl disulfide	3	**~0**	70.8	70.8	0.00980	0.0017	0.0085	1.15	15.3	0.0079	1.24	24.1
Dimethyl sulfide	3	**~0**	56.4	56.4	0.00690	0.0014	0.0076	0.91	9.2	0.0070	0.99	1.4
P-cymene	3	-	200.7	200.7	0.123	0.014	0.1960	0.63	37.2	1.839	0.07	93.3
Ethanethiol	3	**~0**	0.51	0.51	0.00022	0.00006	0.000022	10.00	900.0	-	-	-
Ammonia	3	6.1[d]	267	250.7	1.81	0.22	1.40	1.29	29.3	0.365	4.96	395.9
2,3-butanedione	2	14.4	2.97	2.5	0.00030	0.0001	0.00018	1.67	66.7	-	-	-
Carbon disulfide	2	16.3	211	176.6	0.49	0.14	0.651	0.75	24.7	3.551	0.14	86.2
Beta pinene	3	57.7	404.3	171.0	0.28	0.075	0.187	1.50	49.7	-	-	-
3-Methyl butanol	3	47.5	107.6	56.5	0.026	0.007	0.01	2.60	160.0	-	-	-
Alpha pinene	2	5.5	400.4	378.4	0.22	0.014	0.10	2.20	120.0	4.182	0.05	94.7

[a] N: Measured replicates

[b]Relative losses (%) of compounds within 3 hours of gas storage in nalophan bags. Values in bold were estimated through GC coupled to electrochemical detection (MEDOR), whereas values underlined were measured through GC/MS. Relative losses reported by Hansen et al. (2012) [c] and Sironi et al.(2014)[d] for 3-4 hours of gas sample storage.

[c]Theoretical concentration of gas bags prepared from chemical standards.

[f]Exposure concentration by considering the compounds losses through storage in nalophan bags.

[g]SD: Standard deviation of measured ODT.

[h]Fold difference calculated as the ratio of the measured ODT to the reported ODT values.

[i]Absolute relative deviation (%) calculated as $RD = \frac{|ODT\ measured - ODT\ reported|}{ODT\ reported} * 100\ \%$ (Blazy et al. 2015).

Table 4S. Maximum odor activity values (OAV) of volatiles compounds detected upon aerobic treatment of solid wastes and digestates

	Agricultural waste			Biowaste					Green waste		Sewage sludge		Municipal solid waste		
Chemical compound	**SPS**	**TM**	**ADP**	**FWR**	**FWK**	**FWH**	**ADB**	**ADH**	**YT**	**GB**	**SS**	**ADS**	**MSW**	**MSG**	**ADM**
Acetic acid	7	7	322	2113	4048	3763	21	722	301	126	2841	36	1070	214	150
Propanoic acid			29											2	
Methanol	1<	1<	1<	4	8	1	1<	1	1	1	1<	1<		2	1<
2-Butanol	1<	1<	20		1<		1<	17	2		6		3		
2-Ethyl hexanol	1	1<					1<								
1-Propanol													2		
Ethanol			44	620	676	60		87		10			45	1	1
2-Methyl-1-propanol			24		2657			137							
3-Methyl-1-Butanol				2996		502		238							
1,3-Pentadiene (N.D)															
Benzene	1<	1<					1<								
Toluene	1<	1<					1<								
p-cymene				1315	2555	19		35		232	21			92	242
Styrene							1<								
p,α-Dimethyl styrene				16	12			1		2				1<	1
2-Methyl furan (N.D)															
Pyridine		1													
2-Pentyl furan	2	1					5								
3,5-Dimethylbenzo[b]thiophene								2							
Ethyl acetate				107	109			17					2		
Methyl acetate				75	3			18							
Acetaldehyde			175												
Acetone	1<	1<		13			1<		1<	1<	1<		1<	1<	
2-butanone	1	3	4	567	1	14	1<	71	20	73	7		9		6
3-Methyl-2-butanone	1<	1<					1<								
2-Pentanone	3	6					1<		55				94	40	
3-Methyl-2-pentanone		1<													
2-Hexanone													13		
3-Pentanone										5					
3,3-Dimethyl-2-butanone												1<			
2,3-butanedione				159838											
Methyl thiocyanate (N.D)															
Ammonia	1017	2461	90	2	1<	7	62	1	1	12	129	108	88	1	5
Trimethylamine	57880	1<													
Acetonitrile				1<				1<			1<				
Acetonitrile dimethyl amino															
Ethanethiol					6796	63917		1284	2774	295			75655		355
Methanethiol	212635	145943	7535	305071	119761	53346	8665	12162	126845	10508	149742	20194	418556	24829	459
Hydrogen sulfide	543771	98694	6440	235808	2868	2206	5395	5658	1928	13069	3210	6245	5289	1953	3448

Table 4S. Continued

Chemical compound	SPS	TM	ADP	FWR	FWK	FWH	ADB	ADH	YT	GB	SS	ADS	MSW	MSG	ADM
Dimethyl sulfide	12218	17837	71	206	502	454	283	266	901	1912	8288	1101	3767	161	109
Dimethyl disulfide	14648	27155	87	847	387	374	2338	127	91	598	1253	1516	975	106	451
Sulfur dioxyde				91							1				
Dimethyl trisulfide	35	92					2					349			
Methyl propyl disulfide (N.D)															
Carbon disulfide				33				55							
Dimethyl sulfoxide (N.D)															
Alpha-pinene	7	25	6	140	163	47	145	11	20	2184	12		410	100	568
Camphene	1<	1<					1<			1<				1<	1<
Beta-pinene	1	2	1	96	76	6	33	6	36	15	2			2	
Carene	1<	1<		1	1		1<	1<	1<				1<		
Myrcene		1<		95	488	4	2			225				28	503
Limonene	15	29	170	2313	103510	1199	1063	843	274	860	771	330	4138	146	205
Fenchone		1<					0								
Camphor		1<													
Eucalyptol												32			
Isoterpinolene (N.D)															
Beta-terpinene (N.D)															
Gamma-terpinene										1<				1<	1<
(-)-Thujone										1<				1<	1<
Thymol										17				1	
$SOAV_{max}$	829728	421499	14931	683749	243572	124753	17980	21458	133154	30019	165576	29895	509830	27620	6445

N.D = Not determined, ODT is not reported in the consulted literature.

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Chapter 5: Odor concentration (OC) prediction based on odor activity values (OAV) during composting of solid wastes and digestates

Foreword

In Chapters 3 and 4, we provided a complete characterization of odor emissions upon composting by considering both, analytical and sensory methods. The final aim of these Chapters was to fulfill the urgent need for odor and chemical emission inventories to support odor abatement strategies and odor management plans for this biological process. Even if sensory measurements remain the principal method to evaluate the odor impact of gas emissions on a human panel, there is a growing interest in correlating sensory data to outputs from more cost-effective techniques such as chemical analysis or E-noses. It is important to keep in mind that sensory methods require a trained human panel and extensive sampling and experimental campaigns, thus hindering their daily or often applicability in odor surveys at industrial scale.

The odor concentration (OC in $OU_E\ m^{-3}$) is the odor sensory property more widely correlated to output from instrument-based techniques. This measure of odor detectability is undoubtedly a relevant benchmark value and tool to regulate odors at waste processing facilities around the world and France (the decree of 27/07/12). Nevertheless, OC measurement constitutes only a first step in the determination of odor nuisances, which could be eventually better described and determined by relating these parameters with other important odor dimensions such hedonic tone, odor quality, and odor intensity.

One remarkable approach to predict OC is to construct prediction models based on the odorous potential of the substances comprising the gas mixtures through odor activity values (OAV). Both, univariate and multivariate models based on OAV have shown good performance on predicting OC for some defined odor sources with certain drawbacks such as OC underestimation. For composting process, the link between OAV and OC has been barely addressed in the literature. As proved in Chapter 4, the chemical composition and odor concentration of gas emissions can largely vary according to the organic substrate treated. Despite this strong source of variation, OC prediction models based on OAV during the aerobic treatment have been generally focused on one substrate without validating the suitability of this correlation for different odor sources.

This last Chapter was devoted to analyzing the feasibility of instrumental-based measurements (OAV) to predict OC for odorous gases emitted along the aerobic treatment of six solid waste and three digestates. The results indicated that typical odor surrogates obtained from OAV calculation (OAV_{max} and OAV_{sum}) were moderately regressed against OC and showed lower predictability performances than a partial least squares (PLS) model. The developed PLS model improved the predictability of OC by reducing OC underestimation and approaching predicted values to the 95% confidence interval for olfactometry measurements (EN 13725). Likewise, this last research work corroborated the pivotal role of VSC on odor detectability and evaluated the function of other molecules (i.e., alcohols) in the predictive odor models.

Odor concentration (OC) prediction based on odor activity values (OAV) during composting of solid wastes and digestates

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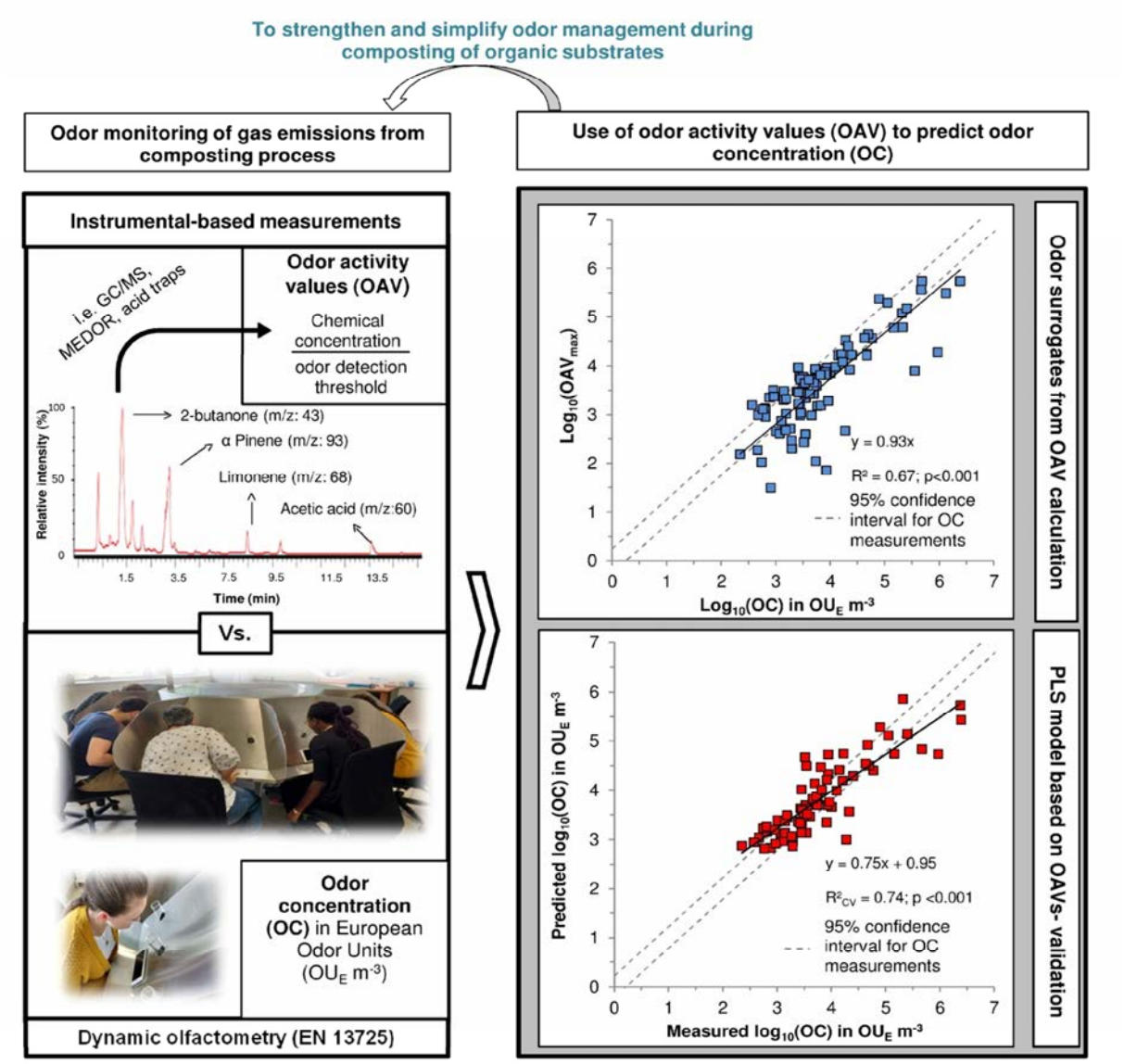
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Abstract

Odor monitoring plays a crucial role in implementing suitable odor mitigation strategies at composting plants. Odor activity value (OAV) analysis is an instrumental-based approach that could simplify and reduce costs of odor monitoring by dynamic olfactometry; yet, the relationship between both methodologies has not been fully explored. In this study, the OAV feasibility to predict odor concentration (OC in OU_E m^{-3}) was assessed during the active composting phase of six solid wastes and three digestates at pilot scale. To this end, 92 gas samples were analyzed by analytical methods (i.e., GC/MS) and dynamic olfactometry (EN 13725). For 22 quantified odorants, OAV was calculated as the ratio of a compound's chemical concentration to its corresponding odor detection threshold (ODT). OAV were then correlated to OC by simple linear and partial least squares (PLS) regressions. The sum of all OAV in the gas samples (OAV_{sum}) and the maximum OAV (OAV_{max}) yielded moderately strong linear correlations against OC (R^2: 0.67 - 0.73), thus providing overall insight into OC trend along composting. A PLS model consisting of weighted OAV of 10 odorants enhanced OC predictions. OAV explained from 74% to 76% of the OC variance throughout the PLS model validation. Furthermore, OC values regressed by the PLS model were less underestimated (7%) than those predicted by OAV_{max} and OAV_{sum} (11-13%). Based on results from the OAV_{max} and PLS regression analysis, hydrogen sulfide, methanethiol, dimethyl sulfide, and dimethyl disulfide were highlighted as the major odor contributors during composting of organic substrates.

Keywords: Odor monitoring, dynamic olfactometry, odor detection thresholds, analytical methods, odor activity values, partial least squares regression.

Graphical abstract



Highlights

- Gas emissions from composting were analyzed by sensory and analytical methods
- OAV provide overall insight into OC trend (R^2: 0.67 - 0.73)
- A PLS regression model enhanced OC predictions through OAV (R^2: 0.74 - 0.76)
- Volatile sulfur compounds were the major odor contributors during composting

1. Introduction

Composting operations are intrinsically associated with odor nuisances that raise public concern about the wellness of plant workers and neighbors from waste treatment units (Tsai et al., 2008; Zhang et al., 2013). To design and support odor mitigation plans, odor emissions are monitored by well-established sensory methods such as dynamic olfactometry. Odor concentration (OC in OU_E m^{-3}) measurement reflects the human detection or perception threshold to gas samples (EN 13725, 2003), but odorants responsible for odor annoyances are not identified. Hence, analytical methods such as GC/MS are used to resolve the main odorants that are present above the methods detection levels (Laor et al., 2014).

Compared to olfactometry, analytical methods are more cost-effective and not affected by human bias response (Wu et al., 2017). Nevertheless, the chemical composition cannot stand as a sole odor indicator. Compounds in the gas mixture can contribute to a different extent to the odor stimuli depending on their odor detection thresholds (ODT) and chemical and physiological interactions (Kim and Park, 2008). At first glance, both sensory and analytical methods are complementary methodologies to face the complex challenge of odor monitoring. Odor activity value (OAV) analysis is an alternative approach that enables to relate chemical concentrations of the compounds to their odorous potential (Capelli et al., 2008; Laor et al., 2014). For a single substance, OAV is an analogous term to odor concentration defined as the ratio of a compound's chemical concentration to its corresponding ODT. Notably, the sum of all individual OAV (OAV_{sum}) and the maximum OAV (OAV_{max}) from odorants within the gas mixtures have been employed in odor assessment for environmental gas samples (Capelli et al., 2008; Parker et al., 2012) and composting gas exhaust (Blazy et al., 2014; Gallego et al., 2012; Schiavon et al., 2017). Understanding the link between OAV and OC is then of crucial importance to simplify odor monitoring through analytical techniques.

Some authors have previously investigated the relationship between OAV and OC. Kim et al. (2008) and Capelli et al. (2012) demonstrated that OC was better correlated to OAV_{sum} than to chemical concentrations. Wu et al. (2017) observed strong linear correlations between OC and OAV_{sum} ($r= 0.91$) during the assessment of landfill gas emission. Likewise, Blazy et al. (2015) obtained encouraging results when using OAV_{max} and OAV_{sum} to predict OC ($R^2> 0.87$) during composting of pig slaughterhouse sludge. However, these studies have also highlighted the underestimation of measured OC through OAV because of the possible presence of interactive odor effects among coexisting odorants (i.e., synergism and antagonism), high variation of ODT datasets, and limitations concerning the number of analyzed gas samples and variation of the odor sources.

Most of the research work evaluating the correlation of OAV and OC has favored the addition of individual OAV in the gas mixture to account for the overall odor emission potential. Parker et al. (2012)

demonstrated that multiple linear regressions (MLR) could reduce the underestimation of OC values predicted (R^2= 0.66-1) by giving a different weight to odorants according to their interactions in the gas sample. Nevertheless, this MLR model also exhibited a low performance upon test set validation (R^2= 0.0-0.5). Based on these previous works, there is a strong need for improving the multivariate prediction of OC through OAV and overcoming the OC underestimation typically reported for simple linear regression models. In the case of the composting process, the chemical composition and odor concentration of gas emissions can largely vary according to the organic substrate treated. Nevertheless, OC prediction models through OAV upon aerobic waste treatment have been generally focused on one substrate without validating the suitability of this correlation for different odor sources.

In this study, we aimed (1) to prove whether OAV can predict OC when composting nine different solid wastes and digestates, (2) to compare the predictability performance of commonly used odor surrogates (OAV_{max} and OAV_{sum}) and a PLS regression model accounting for possible odorants interactions, and (3) to determine the main odor contributors along aerobic treatment of organic substrates based on results from the conducted odor monitoring approach and the regression analysis. To partially reduce the impact of using highly variable ODT dataset, OAV were calculated considering ODT from 15 key odorants measured by the same odor panel that assessed OC.

2. Material and methods

2.1. Compostable substrates and experimental set-up

The active composting phases of six solid wastes and three anaerobically digested substrates (digestates) were simulated at pilot scale over four experimental campaigns from April 2016 to June 2017. Each composting campaign comprised the aerobic treatment of 3 different substrates for approximately 31 days. Compostable substrates were collected from waste treatment sites, restaurants, and farms located in France (Table 1). After being sampled, the organic matrices were stored in plastic bags at -20°C for 1 or 2 weeks. The frozen samples were then thawed at room temperature two days before conducting the composting experiments. If required, substrates were mixed with wood chips of size particle inferior to 40 mm to reduce their bulking density and improve the structure of the compostable material. The ratio bulking agent to substrate and other experimental conditions are listed in Table 2.

Table 1. Sampling places and collected substrates

Waste category	Substrate[a]	Plant feedstock/substrate composition	Sampling place	Acronyms
Agricultural wastes	Pig slurry	Solid fraction of pig slurry	Pig farm	SPS
	Turkey manure	Humidified turkey manure	Turkey farm	TM
	Solid fraction of AD pig slurry	Pig slurry (49.6%), food waste (35.5%) and green waste (14.9%)	Pig farm	ADP
Biowastes	Food waste	Fruits and cooked vegetables, meat, pasta, bread, grease, and fish	Restaurant	FWR
	Food waste	Fruit and vegetable peelings, grease, and coffee ground	Restaurant's kitchen	FWK
	Household food waste	Fruit and vegetable peelings, paper, grease, bread, coffee ground, cooked and raw vegetables, meat, pasta, and bread	Composting plant[b]	FWH
	Solid fraction of AD biowaste from supermarkets	Biowaste from hypermarkets (60%), grease from the food industry (28%) and cereals wastes (12%)	Methanization plant	ADB
	Solid fraction of AD household biowaste	Household biowastes (72%), restaurant biowastes (12%) and green biowaste (12%)	Methanization plant	ADH
Sewage sludge	Sewage sludge	Secondary sludge from WWTP[c]	Composting plant[b]	SS

[a] AD**:** Anaerobically digested substrate; [b] sample collected in the dumping area of composting plants**;** [c]WWTP**:** wastewater treatment plant.

Table 2. Mixture composition and experimental conditions

	Organic substrates								
Mixture composition	**SPS**	**TM**	**ADP**	**FWR**	**FWK**	**FWH**	**ADB**	**ADH**	**SS**
Substrate fresh mass (Kg)	147.6	135.1	126.3	79.9	87.6	55.1	97.9	82.6	72.7
OM content (%FW)[a]	22.8	25.2	24.2	25.9	18.3	28.4	19.1	24.7	11.6
BA fresh mass (kg)[b]	0.0	0.0	0.0	57.1	43.3	48.7	69.0	58.3	78.6
Ratio BA/S[c]	0.0	0.0	0.0	0.7	0.5	0.9	0.7	0.7	1.1
Mixture moisture (%)	68.5	68.8	62.5	49.3	59.3	44.6	69.3	41.9	49.4
Experimental conditions									
Mean aeration rate (L h^{-1} Kg^{-1})	1.2	1.4	3.0	5.3	3.6	4.6	1.9	1.7	5.0
Turning date[d] (days)	14/24	14/24	10/20	10/21	10/21	10/20	14/24	10/21	10/20
Process duration (days)	31.6	31.6	30.9	31.7	31.7	30.9	31.6	31.7	30.9

[a]%FW: percentage in fresh weight, [b]BA: bulking agent, [c]BA/S: ratio BA to substrate on a fresh mass basis.

[d]Turning date: i.e., the compostable mixture was turned at 14 and 24 days of the process.

The compostable mixtures were loaded in 300 L airtight-stainless steel reactors mechanically supplied with air. Composting pilots were covered by metallic lids comprising a gas outlet and a gutter for water condensates. A rotameter (FL-821-V, OMEGA engineering Inc) and a volumetric gas meter (Gallus 2000,

Actaris, Liberty Lake) enabled to daily measure and control air inflows. During the first 24-48 hours of the process, low aeration flow rates (0.9 to 2 L kg^{-1} h^{-1}) were applied to prompt aerobic degradation slowly. This pre-conditioning was followed by the composting material treatment at aeration rates that were kept constant throughout the process (Table 2). The applied aeration rates were selected on the basis of the real operational conditions at the sampling sites and previous research works (de Guardia et al., 2010). Furthermore, the loaded composting material was turned twice after the 10^{th} and 20^{th} day of the process to maintain proper aerobic conditions. Temperature and weight were monitored by Pt100 probes and mass sensors (X201-B, PRECIA MOLEN), respectively. A detailed description of the composting devices is given by Blazy et al. (2014).

2.2. Gas sampling

The gas emitted during the active composting phase of each substrate was first conveyed to a 5 L glass bottle to condensate at room temperature any excess of water vapor and prevent moisture interferences upon sensory and analytical analysis. Water condensates were evidenced in 27% of the sampling days, especially during the first days of composting when hot moist vapor was released. The resulting gas outflow was then channeled toward a set of acid traps, a gas analyzer (O_2/CH_4/CO_2/N_2O URAS 26, ABB, Zurich, Switzerland) and a gas sampling port. The odorous gases were directly sampled into 30 L single-use nalophan bags from 2 to 3 times per week according to the EN13725 (2003). Gas samples were collected punctually for around 10-15 min without observing the presence of any water condensate in that lapse of time. Before conducting gas sampling, it was also assured that not water condensate was present in the glass bottle to avoid possible losses of water-soluble compounds. A total of 92 gas samples were collected and analyzed by both, analytical and sensory methods. Such analyses were shortly conducted from 3 to 6 hours after gas sampling to minimize the impact of storage on compounds recoveries. Odorants can be adsorbed and diffused onto the nalophan bag's surface and react with other molecules during storage, thus resulting in odorant losses (Hansen et al., 2011; Kasper et al., 2018).

2.3. Analytical analysis

Ammonia present in the out-coming gases was trapped in acid traps consisting of two glass impingers filled with 200 mL of sulfuric acid (H_2SO_4 4%). The acids traps were connected in series to the reactors outflows and changed every 48 hours to prevent acid solutions saturation. The gas volume crossing the acid trap system was daily monitored and controlled by a flow meter (FL-821-V, OMEGA engineering Inc) and a volumetric gas counter (Gallus 2000, Actaris, Liberty Lake). The absorbed ammonia (NH_4^+/NH_3) was consequently measured by the modified method NF T90-015-1. This approach involved the steam distillation of ammonia with sodium hydroxide (NaOH, 32%) and boric acid solution (H_3BO_3, 40 g L^{-1}), and its back titration with H_2SO_4 (0.2 N) in an automated titration unit (Gerhardt Vapodest 50s, Germany).

Volatile sulfur compounds (VSC) were assessed according to the norm ISO 6326-2 (1981) by a micro GC coupled to an electrochemical detector (airMEDOR, Chromatotec, France). The VSC analysis enabled to quantify hydrogen sulfide (H_2S), methanethiol (CH_3SH), ethanethiol (CH_3CH_2SH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). To this end, collected gas samples in nalophan bags were directly pumped into a 400 µL loop injection valve at a flow rate of 100 mL min^{-1}. The looped gases were then injected into a capillary column (1.2 m x 1.6 mm x 180 µm) with air as carrier gas at a flow of 4 mL min^{-1}. A column pressure of 230 hPa and a column temperature of 40 °C were held constant throughout the analysis. After separation, VSC were transferred toward an electrochemical cell composed of two platinum electrodes submerged in chromic oxide solution (CrO_3, 10%w). There, analytes underwent REDOX reactions and generated electric potential differences that were measured and recorded. Quantification of VSC was achieved by external calibration (R^2= 0.94-0.99) with high purity compounds (> 98.5%; Sigma-Aldrich and Across Organics) and standard gas cylinders (201±7 ppm and 207±10 ppm standards of H_2S and CH_3SH; Air Liquid). The method detection limits (MDL) were calculated by extrapolating the minimum area measured by MEDOR (1000 unit area) into the performed calibration curves. MDL ranged from 0.015 to 0.06 mg m^{-3} (Table 3).

Volatile organic compounds (VOC) were identified and quantified by a GC/MS (Clarus 500 GC-MS, Perkin Elmer, USA) coupled to a thermal desorption unit (TurboMatrix 550, Perkin Elmer). The gas samples collected in nalophan bags were first adsorbed onto sorbent tubes (Carbotraps 349, Perkin Elmer, USA) at a flow rate of 52 mL min^{-1} with a calibrated vacuum pump (Gilair3, USA). The trapped VOC were then desorbed in the thermal desorption unit at 200°C for 5 min and transferred toward the CG/MS. Once injected, VOC were separated in a capillary column CP-WAX 58 (25m x 0.15 mm x 0.25µm, Varian, USA) with helium as a carrier gas (1 mL min^{-1}) and a column pressure of 310 kPa. The GC oven temperature was first held at 40 °C for 5 min, then increased to 180 °C at 10 °C min^{-1}, and finally maintained at 180 °C for 5 min. VOC were identified by comparing obtained mass spectra (20 to 300 amu) with reference entries from a spectral mass library (NIST 2012, National Institute of Standards and Technology, USA). Moreover, retention times provided a useful criterion for identification if chemical standards were available. The compounds peaks and the identified diagnostic ions (m/z) were acquired and integrated into a full scan and single ion monitoring (SIM) mode. An example of a chromatogram obtained during GC/MS analysis of gas emission is provided in Fig 1S (Supplementary material). An external calibration process (R^2= 0.92-0.99) was applied to quantify VOC with standards (Purity > 98%, suppliers: Fluka, Fisher, Janssen Chemica, Sigma Aldrich, Across Organic and Alfa Aesar). The relative chemical concentrations for 10 VOC were provided by considering a mean calibration response from the entire calibration process (1000). However, only 16 calibrated VOC were considered as input data for developing the statistical models (Table 3). MDL were determined by linear extrapolation of the minimum standard quantity to find a ratio signal to noise equal to 3. The MDL from GC/MS analysis are listed in Table 3.

Because of possible odorant losses due to the gas sampling system, the recovery rates for the main VSC and VOC were determined at 3 and 6 hours of storage. Recovery rates for 17 compounds were evaluated following the methodology explained in Supplementary material 1 (Section 1S). For VOC analysis, the gas sampling system consisted of the nalophan bags, carbotraps, and sampling tubes, whereas VSC were analyzed by pumping directly gas samples from the collected nalophan bag into the GC coupled to an electrochemical detector. Since gas samples were typically analyzed within 3-6 hours, the mean recovery rates during this interval of time (Table 3) were employed to correct the final chemical concentrations. Recovery rates in nalophan bags for trimethylamine, ammonia, propionic acid, ethyl acetate, and dimethyl trisulfide were not measured in this study and then consulted in the literature (Table 3). These reported compounds recoveries were analyzed within 2 to 24 h of storage in nalophan bags (Hansen et al., 2011; Le et al., 2013; Sironi et al., 2014; Van Durme and Werbrouck, 2015).

The final NH_3, VSC and VOC concentrations (Supplementary material 2) were consequently transformed into OAV (Supplementary material 3). For this purpose, the chemical concentration of each quantified substance in the gas samples (mg m^{-3}) was divided by its respective ODT (mg m^{-3}) to yield a dimensionless value (OAV) reflecting the odor potential of the detected compounds. In theory, compounds with OAV superior to one may be involved in odor generation.

In addition to the OAV evaluation, the detection frequency of measured volatile compounds was determined as the number of times in which a single compound was detected divided by the total number of gas samples analyzed. The result of this calculation was expressed on a percentage basis as shown in Supplementary material 2.

2.4. Sensory analysis

The odor concentration (OC) in European odor units (OU_E m^{-3}) of composting gas exhausts was assessed according to the EN 13725 by a dynamic olfactometer ONOSE 8 (Consumaj, Canada). For each sampling day, the results of three or two analyzed gas samples were averaged to yield the OC geometric mean. In case of extreme high OC, odor gases were pre-diluted 100 folds by injecting a known volume of the gas sample with a tight gas syringe (SGE, Australia) into a gas bag that contained a defined volume of air (Blazy et al., 2015). The olfactometer was equipped with calibrated air mass flow controllers that delivered precise air volumes to prepare diluted samples. The effect of the gas-tight syringe on VSC recoveries was assessed by injecting standard gases (H_2S and CH_3SH) into a gas sample containing 30 L of dry air (Supplementary material 1, section 2S). The recovery rates were on average 109±15%, thus demonstrating a limited influence of transferring the gas sample for VSC. Kim and Kim (2015) also reported low sorptive losses (2.6%) for aldehyde, ketone, ester, alcohols, and aromatic hydrocarbon when using tight gas syringe as transfer media, but high losses for carboxylic acids and cresols (18-64%).

The raw or pre-diluted gas samples were presented in an ascending concentration order to a group of minimum five calibrated panelists to determine the dilution factor in which half of the tested panel perceived an odor stimulus. Using ONOSE 8, the gas samples were automatically diluted with analytical grade air at a step factor of 2 and a dilution range varying from $2^{2.7}$ to $2^{15.7}$. The OC was then assessed in a force choice mode involving the detection of an odor stimulus from odorless gas in a three-port sniffing station. Each tested gas sample was measured three times, but only results from the last two presentations were used to calculate the OC geometric mean. Panelist calibration with n-butanol (Sigma-Aldrich, 99.9%) showed a mean ODT of 148 ± 84 μg m^{-3}, thus complying with EN13725 standards (62-246 μg m^{-3}).

2.4.1. Odor detection thresholds (ODT)

ODT can differ by several orders of magnitude in reported datasets (Parker et al., 2012; Wu et al., 2017). To partially reduce the impact of using highly variable ODT on OAV calculation, 15 ODT were measured by dynamic olfactometry (EN 13725, 2003) with the same calibrated panel that assessed the gas samples collected along the composting experiments. The measured ODT included some of the most frequently detected and odorous compounds such as VSC and trimethylamine (Table 3). Firstly, gas samples of the target compounds were prepared in replicates by injecting liquid and gas standards into nalophan bags containing a known volume of analytical grade air. Injected substances were volatilized and stored at room temperature for around 3 hours. The initial compounds concentrations were computed as the ratio of the mass injected into the final gas sample volume. These chemical concentrations ranged from 0.4 to 404 mg m^{-3}. Nevertheless, the exposure concentration (C_0) at the time of sensory analysis were calculated by considering the relative losses of analyzed substances during three hours of storage time in nalophan bags (Supplementary material 1, Table 3S). The prepared gas sample replicates (from 2 to 5) were then diluted in ascending concentration order at a step factor of two with analytical grade air to be assessed for a group of minimum five calibrated assessors. For each replicate, the dilution factor at 50% (Z_{50}) of odor detection threshold was determined in a forced choice mode. The ODT for each substance (ODT_i in mg m^{-3}) was finally computed as the ratio of the exposure concentration (C_0 in mg m^{-3}) in the nalophan bag to its measured Z_{50} (dimensionless) as seen in Eq. 1:

$$ODT_i = \frac{C_0}{Z_{50}} \quad \text{Eq. 1}$$

Although all construction criteria as per EN 13725 are met, olfactometers can substantially affect the recovery of certain molecules. Hansen et al. (2013) demonstrated that recoveries of carboxylic acids, trimethylamine, and 3-methylphenol are largely affected by the dynamic dilutions without even reaching the expected concentration at a 60 seconds pulse (presentation time). Hence, further studies are necessary to correct the measured ODT by taking into account the recovery rates of these substances in the employed olfactometer.

The ODT reported by Nagata (2003) were preferably used through OAV calculation when experimental ODT were not available. Five substances were not found in Nagata's ODT dataset (Table 3) and then consulted in Van Gemert (2011) compilation by considering the most recent ODT values.

2.5. Data analysis

The measured OC and OAV were correlated to examine the relevance of OAV as a predictor for OC through univariate and multivariate linear regression models. Since OC and OAV are log-normally distributed (Akdeniz et al., 2012; Hansen et al., 2016), both variables were log-transformed before performing the correlation analysis. This scaling process limited background noises caused by irrelevant variation and highlighted correlation patterns among variables. The non-detected values were considered as missing values or empty cells when performing regressions and descriptive statistical analysis.

As a first logical step, OC was initially compared by simple linear regression with two odor surrogates derived from OAV calculation: OAV_{max} (Blazy et al., 2015; Kim and Kim, 2014) and OAV_{sum} (Parker et al., 2012a; Wu et al., 2016). For a gas mixture containing several volatile compounds, OAV_{max} was defined as the highest OAV linked to the most odorous compounds within the gas mixture, whereas OAV_{sum} was obtained by the addition of OAV of all the compounds detected. Both odor coefficients were determined for each analyzed gas sample (Supplementary material 3).

Besides testing univariate correlations, a partial least squares regression (PLS) was performed in The Unscrambler X version 10.5 (CAMO, Norway) to predict OC based on OAV of all the detected odorants as explanatory variables. Once log transformed, the dataset consisting of 92 gas samples was divided into a training and test set (Supplementary material 4). Both datasets contained representative input from analyzed gas emissions upon composting of the nine substrates studied. The missing values imputation during model construction was conducted by the modified nonlinear iterative partial least squares regression algorithm (NIPALS). Calibration models were developed based on the training set and validated by segmented cross-validation and test set validation. Samples included in the cross-validation segments were randomly selected as shown in Supplementary material 4. The coefficient of determination (R^2), the root mean square error of cross-validation (RMSECV) and test set validation (RMSEP) enabled to assess the models' performance and robustness (Gutiérrez et al., 2015). An initial PLS model was developed with 22 quantified odorants. Thereafter, an iterative variable selection process was conducted by removing not statistically significant variables according to their Jack-knifing uncertainty estimates. In this approach, the uncertainty variance from PLS regression coefficients was estimated throughout the cross-validation process (Hansen et al., 2016).

The percentage of predicted OC values falling inside the 95% confidence interval for the measured OC was also calculated to assess the reliability of the proposed univariate and multivariate correlations in compliance with EN 13725. The 95% confidence interval of odor concentration (OC_{int}) was computed by Eq.2.

$$OC - t * \frac{S_r}{\sqrt{n}} \leq OC_{int} \leq OC + t * \frac{S_r}{\sqrt{n}} \quad \text{Eq.2}$$

Where OC is the measured OC logarithmically transformed; t is the Student's t-factor (t= 2 for a confidence interval of 95%), S_r is the standard deviation from laboratory repeatability (0.1721), and n is the average number of tested gas samples (n= 2.5).

Finally, the absolute Relative Deviation (RD) from predicted OC values standing outside the 95% confidence interval were determined (Blazy et al., 2015). This measure quantified the dispersion of predicted OC by comparing it with the closest interval boundary (OC_{int}) on a percentage basis (Eq.3). Both terms were logarithmically transformed prior calculation.

$$RD = \frac{|OC_{predicted} - OC_{int}|}{OC_{int}} * 100\ \% \quad \text{Eq.3}$$

Absolute RDs resulting upon linear (OAV_{sum} and OAV_{max}) and PLS regressions were drawn in a box plot to further analyze the distributional characteristic of RDs and predictability accuracy according to EN 13725.

3. Results and discussion

3.1. Odorants released during the active composting phase

A total of 22 quantified volatile compounds showed concentrations that exceeded at least once their ODT (Supplementary material 2) and yielded OAV superior to one (Supplementary material 3). These critical odorants and their median chemical concentrations are listed in Table 3. The interquartile range (IQR) for the compounds chemical concentrations and OC are also presented by considering the 50% of data spread between the first quartile (Q_1) and third quartile (Q_3). Despite the differences in process conditions and organic matrices nature, some odorants were frequently emitted throughout the composting experiments. In increasing order, the compounds displaying detection frequencies higher than 70% were methanol, ammonia, hydrogen sulfide, alpha-pinene, dimethyl disulfide, acetic acid, and limonene. Ammonia and acetic acid have been commonly detected in emissions from waste treatment facilities (Kim et al. 2008) and food waste composting plants (Tsai et al., 2008). Limonene and alpha-pinene emissions have been associated to the presence of vegetable feedstock and bulking agent upon aerobic treatment of biowaste (Cerda et al., 2018), MSW (Maulini-Duran et al., 2013; Scaglia et al., 2011) and green waste (Gutiérrez et al. 2014). Similarly, dimethyl disulfide and hydrogen sulfide have been identified as significant odor contributors along aerobic treatment of sewage sludge (Schiavon et al., 2017; Zhu et al., 2016) and MSW (Scaglia et al., 2011; Zhang et al., 2013).

Diverse odor emissions peaks were observed when conducting the active composting phase of each compostable substrate (Supplementary material 5). Peak odor emissions were commonly present after starting the aeration process and performing the turning of compostable substrates at around the 10^{th} and 20^{th} day of the process. The OC measured along substrates aerobic treatment (median: 4381 $OU_E\ m^{-3}$, IQR: 1962-17323 $OU_E\ m^{-3}$) was within the same order of magnitude to those reported upon composting of organic fraction of MSW (OC range: 300- 22000 $OU_E\ m^{-3}$) (Gutiérrez et al., 2014). Additionally, extreme OC values were episodically detected at the pilots' outlet as confirmed by the maximum ($2.44\ 10^6\ OU_E\ m^{-3}$) and the 95^{th} percentile of OC ($4.7\ 10^5\ OU_E\ m^{-3}$). Blazy et al. (2015) also determined extreme OC (range OC: 304 - $4\ 10^6\ OU_E\ m^{-3}$) when analyzing point source emissions from pig slaughterhouse sludge composting.

Table 3. Summary of main odorants emitted upon composting process of 9 organic matrices

Chemical compound	m/z[a]	Calibration factor[b]	Recovery rate (%)	MDL[g] (mg m^{-3})	ODT[i] (mg m^{-3})	Concentration (mg m^{-3})[j]					Detection frequency (%)[k]
						Median	**Q_1**	**Q_3**	**Min.**	**Max.**	
Acetic acid	60	184	70 ± 10	0.00074	**0.019**	1.2	0.18	6.4	0.0009	108.4	85.2
Propionic acid	74	*1000*	74 ± 11[c]	-	0.017	0.66	-	-	-	-	0.9
Methanol	31	1004	100 ± 13	0.00556	43	1.1	0.11	7.6	0.010	348.3	72.2
2-Butanol	45	2914	61 ± 5	0.00037	0.66	0.27	0.027	5.1	0.0053	22.0	22.2
Ethanol	31	2274	106 ± 15	0.0042	0.99	2.3	0.20	24.8	0.0066	629.1	50.9
2-Methyl-1-propanol	43	*1000*	-	-	0.033	0.79	0.13	3.7	0.010	87.7	12.0
3-Methyl-1-Butanol	55	686	57 ± 6	0.00093	**0.026**	3.4	0.50	11.6	0.015	137.8	25.9
P-cymene	119	1480	-	0.02315	**0.12**	1.2	0.25	3.0	0.024	314.2	46.3
p.α-Dimethylstyrene	132	*1000*	-	-	*1.33*	0.17	0.071	0.60	0.015	21.6	28.7
Ethyl acetate	61	266	90[d]	-	3.14	21.9	4.42	306.0	0.0067	569.7	15.7
Methyl acetate	43	*1000*	-	-	5.1	55.4	8.04	161.1	1.7	383.6	10.2
Acetone	58	462	77 ± 17	0.00056	101	0.21	0.007	4.4	0.0012	34.8	25.0
2-butanone	72	2537	82 ± 13	0.00037	1.3	0.13	0.014	3.8	0.00064	896.8	57.4
2-Pentanone	86	640	-	-	0.098	0.025	0.010	0.094	0.00007	0.56	14.8
2.3-butanedione	43	862	80 ± 8	0.00074	**0.00030**	7.6	5.40	33.0	3.2	58.4	2.8
Ammonia	-	-	89 ± 6[e]	0.29[h]	**1.81**	18	1.9	183.9	0.38	5001	72.2
Trimethylamine	58	775	81 ± 25[c]	0.013	**0.00073**	45.9	15.2	49.3	0.14	143.3	5.6
Pyridine	79	*1000*	-	-	0.2	0.032	0.019	0.061	0.009	0.29	4.6
2-Pentyl furan	81	*1000*	-	-	*0.019*	0.010	0.0027	0.031	0.0022	0.089	6.5
Ethanethiol	-	63274	102 ± 1	0.015[h]	**0.00022**	1.5	0.89	7.5	0.28	13.4	2.8
Methanethiol	-	70399	104 ± 1	0.0225[h]	**0.00021**	1.6	0.36	5.5	0.026	64.1	58.3
Hydrogen sulfide	-	36212	105 ± 4	0.035[h]	**0.00047**	1.2	0.45	3.6	0.055	255.6	75.0
Dimethyl sulfide	-	41412	104 ± 1	0.06[h]	**0.0069**	0.99	0.28	3.0	0.062	123.1	50.0
Dimethyl disulfide	-	41923	110 ± 1	0.032[h]	**0.0098**	0.88	0.21	3.7	0.032	266.1	77.8
Sulfur dioxide	64	*1000*	-	-	2.3	2.8	1.86	28.0	0.17	208.9	6.5
Dimethyl trisulfide	126	*1000*	90[f]	-	*0.014*	0.028	0.0064	0.15	0.00033	1.4	15.7
Carbon disulfide	72	*1000*	81 ± 4	-	**0.49**	0.24	0.092	7.3	0.052	32.8	14.8
Alpha-pinene	93	906	76 ± 26	0.017	**0.22**	1.1	0.36	5.11	0.023	47.1	76.9
Beta-pinene	93	500	51 ± 12	0.039	**0.28**	0.91	0.31	3.1	0.052	53.0	54.6
Carene	93	689	-	0.0015	*9.3*	0.70	0.10	3.3	0.0019	13.5	36.1
Myrcene	93	*1000*	-	-	*0.14*	0.063	0.0063	0.49	0.00011	68.3	26.9
Limonene	68	334	105 ± 0.1	0.016	**0.18**	7.2	0.55	34.9	0.037	18942	86.1
OC (OU_E m^{-3})	-	-	-	-	-	4381	1963	17323	223.9	2.44 10^6	-

[b]Calibration factor. Compounds with a calibration coefficient of *1000* were semi-quantified and not included in the statistical models.
Mean recovery rates in nalophan bags after 3-6 h of storage. Recovery rates as reported by [c]Hansen et al. (2012), [d]Van Durme and Werbrouck (2015), [e]Sironi et al. (2014), and [f]Le et al. (2013).
[g]MDL: method detection limit. [h]MDL for GC coupled to electrochemical detection (MEDOR) and acid traps (ammonia).
[i]Odor detection thresholds (ODT) in bold were measured by dynamic olfactometry. Underlined ODT were reported by Nagata (2003), and ODT in italics were consulted in Van Gemert's (2011) compilation.
[j]Q_1: 25th Percentile and Q_3: 75th Percentile; IQR: Interquartile range from Q1 to Q3.
[k] Detection frequency of odorants upon instrumental analysis of 92 gas samples.

The OAV for VSC, Trimethylamine (TMA), and 2-3 butanedione were underestimated at low concentrations because they presented lower ODT than their respective MDL (Table 3). Previous studies have reported the negative impact of this instrumental limitation on OC prediction through OAV (Laor et al., 2014; Parker et al., 2012b). Hence, to corroborate the OAV underestimation levels, MDL were divided by their corresponding ODT (Blazy et al., 2015). In decreasing order, the substances most likely underestimated were CH_3SH, TMA, H_2S, ethanethiol, DMS, DMDS, and 2-3 butanedione. The obtained underestimation levels ranged from 107 to 2, with a cumulative underestimation of 353. However, these values were relatively low when compared to the median OC (4381 OU_E m^{-3}, IQR: 1962-8742 OU_E m^{-3}). This error on OAV calculation could have principally affected odor prediction for gas samples accounting for low odor and chemical concentration levels. To observe the impact of OAV underestimation on the determined odor surrogates (OAV_{max} and OAV_{sum}), the underestimation errors were added and compared with the initial values through their relative deviations (Blazy et al. 2015) as shown in Supplementary material 3. The mean relative deviations for OAV_{max} and OAV_{sum} were 0.6% and 10%, respectively, thus demonstrating a limited influence of OAV underestimation when computing these odor surrogates. Using a GC coupled to Pulsed Flame Photometric Detector (PFPD) could drastically increase the VSC detectability and reduce OAV underestimation. MDL reported for GC/PFPD are in the order of 0.01 to 0.03 μg m^{-3} (He et al., 2018; Kim and Kim, 2014) which are notably lower than the measured ODT for VSC (Table 3).

3.2. Prediction of odor concentration through OAV_{max} and OAV_{sum}

The maximum OAV (OAV_{max}) in the gas mixtures are commonly used to identify and monitor the odorants contributing the most to odor annoyance (Blazy et al., 2015; Sivret et al., 2016; Wu et al., 2017). Hence, the relationship between OAV_{max} and OC was assessed (Fig. 1.A) by considering that the leading odorants presenting OAV_{max} were mainly responsible for the odor stimulus perceived by the human panel upon sensory analysis. For the analyzed gas samples, OAV_{max} was typically displayed by H_2S (51.1%), CH_3SH (33.7%), limonene (4.3%), acetic acid (4.3%), and other compounds such as DMS (2.2%), 2,3-butanedione (2.2%), and ethanethiol (2.2%). In other words, VSC were the major odor contributors, accounting for 89% of the odorants exhibiting OAV_{max} during aerobic treatment of solid wastes and digestates. In line with Mochalski et al. (2009) and Hansen et al. (2012), VSC presented very high recoveries upon storage in nalophan bags (Table 3). Such fact could have led to identifying VSC as the most odorous compounds in emission from composting. However, OC and OAV_{max} were possibly correlated because both parameters were measured under the same gas sampling and storage conditions.

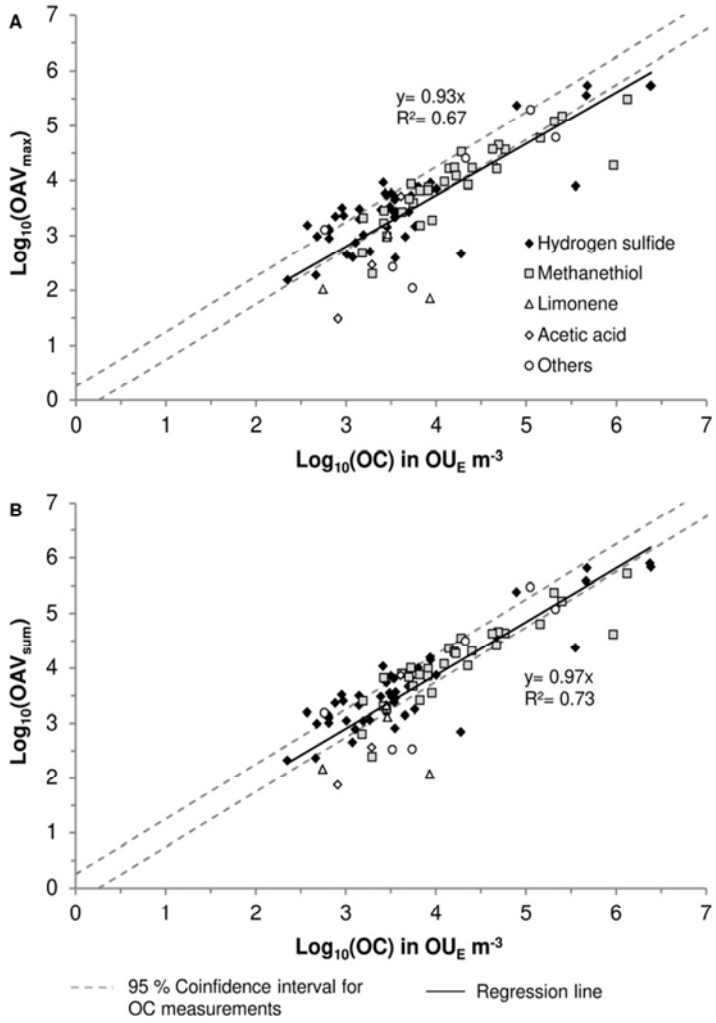


Fig. 1. Linear correlations between (**A**) the maximum OAV (OAV_{max}) and odor concentration (OC), and (**B**) the sum of individual OAV (OAV_{sum}) and OC for 92 gas samples from the active composting phase of 9 organic matrices. OAV and OC were log-transformed. Main compounds displaying the OAV_{max} are indicated for all gas samples in both correlations. The regression lines are depicted as full lines, and the dashed lines represent the 95% confidence intervals for OC measurements

As depicted in Fig 1.A, 67% of the measured OC variance was explained by the OAV_{max} ($p<0.0001$). The resulting function Log (OAV_{max})= 0.93 Log (OC) was relatively close to the 95% confidence interval and featured similarly to the ideal assumption of Log (OAV_{max}) being equal to Log (OC). However, only 43% of the predicted OC through OAV_{max} fell inside of the 95% confidence interval for the OC measurements. Particularly, an underestimation of OC predictions was observed for 63% of the analyzed gas samples when using OAV_{max} as OC surrogate. Predicted OC was on average 13% inferior to the reference values obtained by dynamic olfactometry. The correlation between OC and OAV_{max} could have been hindered by the presence of synergistic, antagonistic and even neutralizing interactive effects among odorants coexisting within the gas samples. Previous studies have proved that odorant interactions can regulate and influence the final odor perception (Kim and Park, 2008; Wu et al., 2015; Zahn et al., 2001).

For instance, OC prediction through OAV_{max} could have been underestimated because the synergism among molecules was neglected. Another important source of error for this correlation is the uncertainties associated with the human panel responses during dynamic olfactometry (Klarenbeek et al., 2014; Laor et al., 2014; Wu et al., 2017). Despite being calibrated with n-butanol, odor sensitivity within assessors can widely differ, bringing some variation which is not possibly explained by the chemical composition in the gas mixture.

Furthermore, the olfactometer could have also affected the recoveries of certain compounds upon sensory test. As explained by (Hansen et al., 2013), the concentrations in the sniffing port for sulfur compounds, carboxylic acids, trimethylamine, and 3-methylphenol can be lower than expected, thus resulting in an underestimation of OC. Despite such inherent complexity arising from measuring odors in environmental gas samples, the moderately strong linear correlation (R^2= 0.67, $p<0.0001$) obtained between OAV_{max} and OC suggests that OAV_{max} could provide a preliminary estimation of odor nuisances during composting of solid waste and digestates with an expected level of uncertainty.

The correlation between OAV_{sum} and OC yielded a regression line performing similarly to the one obtained for OAV_{max} (Fig. 1B). OAV_{sum} explained the OC variance with a slight increase on the coefficient of determination (R^2: 0.73, $p<0.0001$); yet, a certain degree of uncertainty for OC predictions was still present with only 44% of the predicted values laying inside of the 95% confidence interval for OC measurements. OC predicted by OAV_{sum} were on average 11% inferior to the OC measured. Besides leading to similar linear regression models with OC, OAV_{max} and OAV_{sum} followed similar trends all along the composting process (Supplementary material 5). In fact, the mean ratio between OAV_{max} and OAV_{sum} was 0.77, suggesting that most of the OAV_{sum} magnitudes principally come from the leading odorants responsible for OAV_{max} in the gas samples.

Although OAV_{max} could be a preliminary tool for odor monitoring and management, it is not frequently addressed in the literature. Blazy et al. (2015) demonstrated that OAV_{max} was linearly correlated with OC (R^2: 0.90) during composting of pig slaughterhouse sludge. Similarly, Kim and Kim (2014) observed a strong linear relationship between OC and OAV_{max} (R^2= 0.91) for fresh food material after categorizing in different food types (Kim and Kim, 2014). More research is therefore needed to support the suitability of OAV_{max} approach on different biological treatments and process involving odor emissions. Focusing on target odorants exhibiting OAV_{max} can upgrade and lower costs at the regular odor survey programs. According to our results, a regular VSC monitoring could play an essential role in accomplishing proper odor management at composting plants.

In contrast to OAV_{max}, the relationship between OC and OAV_{sum} has been relatively more studied. For instance, strong linear correlations with R^2 ranging from 0.84-0.91 were attained when evaluating odor gas emission from pig slaughterhouse-sludge composting (Blazy et al., 2015), industrial sites (Capelli et al.,

2012; Kim and Park, 2008) and a landfill (Wu et al., 2017). Despite reporting good linear models, Capelli et al. (2012) and Wu et al. (2017) also observed that OAV_{sum} was inferior to the measured OC by some orders of magnitude. To partially solve this discrepancy, a scaling factor was used by Wu et al. (2017) to predict OC through OAV_{sum}. Likewise, Parker et al. (2012) found that OC from gas emissions of animal buildings was underestimated from 2 to 3 times by OAV_{sum} in a simple linear model (R^2:0.16 to 0.52), thus developing multiple linear regressions (MLR) to weight compounds OAV according to their odor contribution. In the next section, a PLS regression was explored to prove if weighting OAV on a multivariate model could improve OC prediction.

3.3. Modeling OC and OAV by a Partial Least Squares (PLS) regression

A PLS regression analysis was first developed and validated by considering 22 quantified odorants. As summarized in Table 4, this initial PLS model presented moderate predictability accuracy upon cross-validation and test set validation (R^2_{CV}:0.67; R^2_{Predi}: 0.67). The cause of this shortcoming was the presence of irrelevant variables and background noises that interfered in OC prediction. To seek a simpler and more robust PLS regression model, some authors have demonstrated the importance of selecting the main odor contributors and explanatory variables (Campo et al., 2005). Hence, a second model was built by removing useless variables not statistically significant according to Jack–knifing approach. The variable removal was conducted in an iterative process consisting of eliminating one by one the target variables and verifying the resulting model robustness at each round. The final PLS model, including ten relevant odorants, explained 74% of the OC variance upon cross-validation and 76% of the OC variance through test set validation. As seen in Table 4, the RMSECV and RMSEP were consequently lowered while applying this variable selection approach.

Poor OC predictions based on OAV have been reported during the test set validation (R^2_{pred}: 0.0-0.53) of a multiple linear regression (MLR) model (Parker et al., 2012a). In contrast to PLS regression, MLR models can be misleading if there is collinearity or autocorrelation among the explanatory variables (Hobbs et al., 2001). The used training test showed residuals autocorrelation (Durbin-Watson test: $d=1.3$, $p<0.05$), thus highlighting the suitability of PLS regression to model OC based on OAV from odorants. As a result, a reliable PLS model performing well upon test set validation (R^2_{Pred}: 0.76) was obtained. Hansel et al. (2016) also demonstrated the PLS regression analysis feasibility to predict OC (R^2_{pred}:0.77) when correlating in-situ analytical and sensory measurements from pig production facilities. Three-PLS components models were chosen in this study to reach the lowest residual variance along the cross-validation process (Supplementary material 6).

Table 4. Quality parameters of the developed PLS models to predict odor concentration (OC, $OU_E\ m^{-3}$) based on OAV of odorants detected by analytical means

Model[a]	N[b]	Range Log_{10}(OC)	R^2_{CV}	RMSECV[c]	R^2_{Pred}	RMSEP[c]
A (22 odorants)	72	2.3 - 6.4	0.67	0.50	0.67	0.55
B (10 odorants)	72	2.3 - 6.4	0.74	0.44	0.76	0.48

[a] PLS regression models with 3-PLS components. OC and OAV were log-transformed. A: All quantified odorants; B: Final model refined by an iterative selection of variables considering Jack-knifing uncertainty estimates.

[b] Training set's sample size.

[c] Root means square error of cross-validation (CV) and test set validation (P). Test set's sample size was 20.

The relationships among the ten explanatory variables included in the final PLS model and the response (OC) were assessed in a correlation loading plot (Fig. 2). The 2D- correlation loading plot was displayed for the first two PLS components describing 75% of the OC variance (Y-matrix) and 69% of the OAV variance (X-matrix). The zone between the inner and outer ellipses in Fig. 2 indicates a range from 50% up to 100% of explained variance. The OC and OAV from odorants used in the model were placed inside this zone, thus reflecting the high contribution of these variables when explaining data variation by the first two PLS components. Notably, VSC were positively correlated to OC as proved by the closeness of these variables in the plot's upper right quadrant (Fig.2). Alcohols, ketones, and terpenes were clustered in the plot's lower right quadrant which may be linked to a specific type of effect exerted by these chemical compounds on odor perception. Even if direct causal relationships between OAV and measured OC cannot be only proved by statistical means, an overall insight into major odor contributors was obtained by comparing results from the OAV_{max} approach and the performed PLS analysis (Hansen et al., 2016; Parker et al., 2012b). Hence, VSC were considered as the main OC contributors and predictors for composting gas emissions because of their significant contribution to OAV_{max} (section 3.2) and their strong correlations with OC along the multivariate regression analysis.

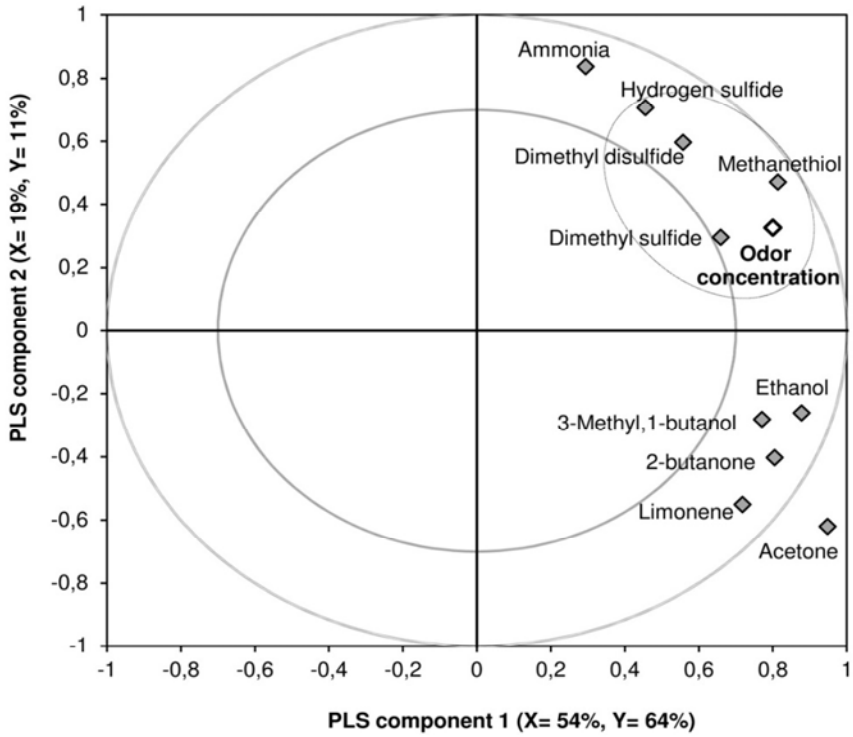


Fig. 2. Correlation loadings plot for a developed partial least squares (PLS) model to predict odor concentration (OC in OU_E m^{-3}) through odor activity values (OAV). OC and OAV were log-transformed. The first two PLS components explained 75% of the OC (Y) variance during model calibration

The relevance of VSC on the OC prediction model was also confirmed by inspecting the size and the statistical significance of their regression coefficients (Fig. 3). In decreasing order, H_2S, CH_3SH, and DMDS exhibited statistically significant regression coefficients ($p<0.05$) that had a strong influence on the performance of the OC prediction model. Likewise, 2-butanone and ammonia accounted for statistically significant regression coefficients ($p<0.05$). 2-butanone is a by-product of aerobic metabolism which has been included as an explanatory variable in previous PLS models to predict OC in an MSW composting plant (Gutiérrez et al., 2015). Although ammonia accounts for a relatively high ODT (Table 3), 70% of the analyzed gas emission from composting containing NH_3 showed levels that exceeded this measured ODT (Supplementary material 3). This fact may explain the ammonia relevance of the developed PLS model. Furthermore, this weak base could have significantly affected the acid-base balance of the air pollutants present in the gas exhausts (Hobbs et al., 2001). For instance, ammonia can interact with sulfide and H_2S to form air particles which may affect the final composition of the odor plumes and consequently their odor impact (Zahn et al., 2001).

Surprisingly, alcohols were the only chemical family exhibiting negative regression coefficients. This result may suggest a possible antagonistic interactive effect of 3-methyl-1-butanol and ethanol on odor perception; yet, sensory experiments must be conducted to validate such an assumption. The antagonistic effect of these alcohols on odor detectability have not been previously discussed in the literature, but

other hydroxyls containing molecules such as phenol and 4-ethyl-phenol were identified as antagonist odorants upon sensory measurements of gas samples from swine effluents (Zahn et al., 2001) and a waste disposal plant (Wu et al., 2015).

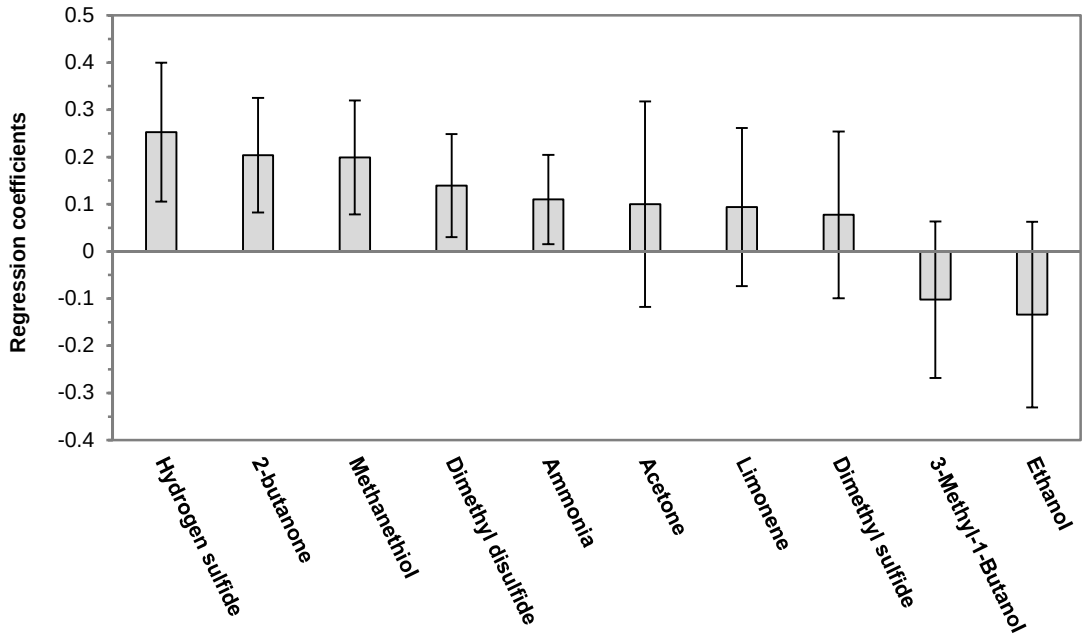


Fig. 3. Regression coefficients for the final partial least squares (PLS) regression model to predict odor concentration (OC in OU_E m^{-3}) through odor activity values (OAV). OC and OAV were log-transformed to build a 3-PLS components model. Error bars represent the uncertainty estimates calculated by the jack-knifing approach

For the cross-validated PLS model, 44% of the predicted OC values were inside the 95% interval confidence as per EN 13725 (Fig. 4); that is, the reliability of OC prediction in compliance to EN 13725 was similar to those found by the simple linear models developed through OAV_{max} and OAV_{sum} (43-44%). When applying the PLS model to predict OC, 50% of gas samples exhibited an underestimation of OC values. OC predictions by PLS were on average 7% inferior to the measured values. The developed PLS model enabled to predict better the measured OC with less average underestimation than OAV_{max} (13%) and OAV_{sum} (11%). In the case of predicted OC along test set validation (Fig. 5), only 20% of the predictions fell inside the 95% confidence interval. However, 92% of the predicted points matched with the OC confidence interval boundaries when considering the prediction error (RMSEP= ±0.48). In the next section, the closeness of predicted OC to the confidence interval boundaries was further analyzed by the absolute relative deviation (RDs).

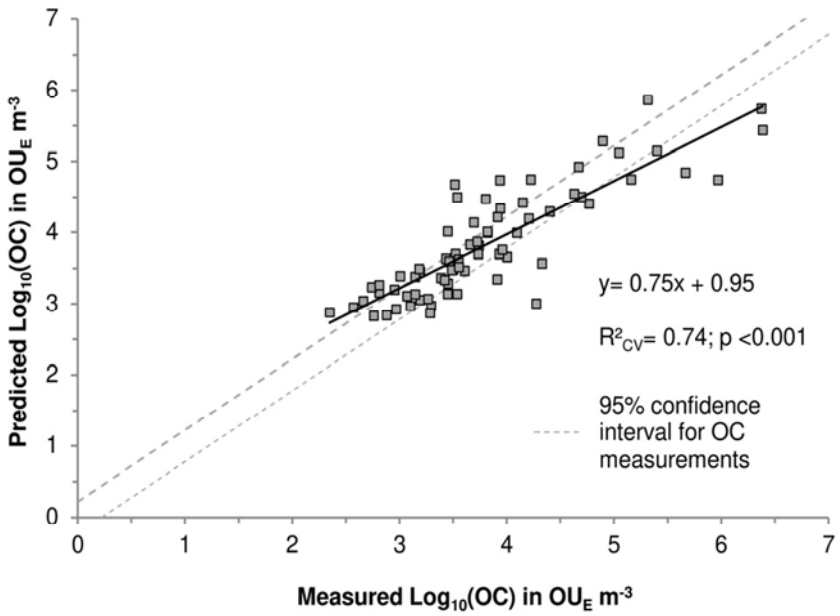


Fig. 4. Comparison between the measured odor concentration (OC in OU_E m^{-3}) and the predicted OC. A partial least squares (PLS) regression model with three components was validated by cross-validation (N= 72). OC was predicted by the weighted odor activity values (OAV) of 10 odorants. OC and OAV were log-transformed

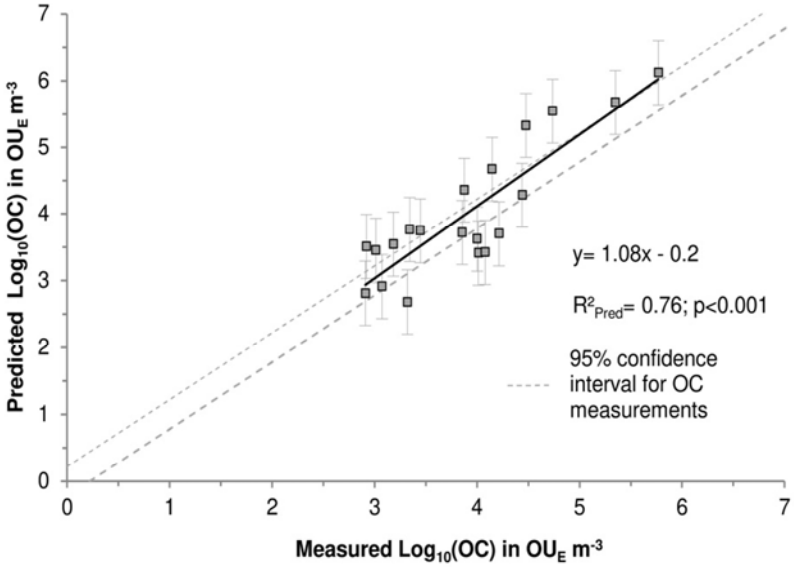


Fig. 5. Test set validation (n= 20) of the developed PLS model with three components. Odor concentration (OC in OU_E m^{-3}) was predicted by the weighted odor activity values (OAV) of 10 odorants. OC and OAV were logarithmically transformed. Root mean square errors of test set validation (RMSEP) are depicted for each prediction

The observed differences between the predicted OC through the PLS model and measured OC (unexplained variance: 24-26%) are likely associated with the measurement errors derived from the

analytical and sensory techniques, but also the gas sampling system. Despite being previously calibrated with n-butanol, the human panel evaluating gas samples through dynamic olfactometry can bias the reference OC measurements due to the intrinsic variation in assessor responses and odor sensitivity (Gutiérrez et al., 2015; Klarenbeek et al., 2014). Moreover, some unavoidable uncertainties are produced when performing the dynamic dilutions in a step factor of two by the olfactometer (Hansen et al., 2016). As proved by the recovery rates in Table 3, another important source of error was the gas sampling system involving the use of nalophan bags and adsorbents tubes (carbotraps) which caused compound losses, a decrease on odorant recoveries and finally underestimations of the chemical concentrations used to compute OAV. Such drawback could have led to neglect the odor impact of extremely odorous compounds that have been reported to exhibit meager recovery rates in nalophan bags such as phenols and indoles (Hansen et al., 2011). This fact was documented by Hansen et al., 2012 while predicting OC through a PLS model based on chemical concentrations in pig production facilities. In this study, indoles were not included in the multivariate model because of their poor recovery rates (48-60%) in nalophan bags and their relevance on odor generation could not be assessed.

3.4. Performance of prediction models based on absolute relative deviations (RDs)

The dispersion of predicted OC values standing outside the 95% confidence interval was assessed by the absolute relative deviations (RDs). In general, the RDs medians ranged from 5% to 7% (Fig. 6), indicating that 50% of the OC predictions falling outside the 95% interval confidence were very close to the interval boundaries for both, univariate and multivariate correlations. However, RDs distributions for OAV_{max} and OAV_{sum} were relatively more spread than for PLS regressions. The RDs range for OAV_{max} and OAV_{sum} varied from 0.7% up to 50%, whereas PLS regression had narrower RDs ranges fluctuating between 0.2% and 26%. Furthermore, OC surrogates were more sensitive to the presence of outliers representing highly dispersed points to the confidence interval boundaries. For instance, OAV_{max} had nine outliers above 20%, while the cross-validated PLS model presented just two. These results indicate that OC predictions yielded by the PLS model (Table 4, model B) were less dispersed from the 95% interval confidence boundaries than the ones obtained by the odor surrogates.

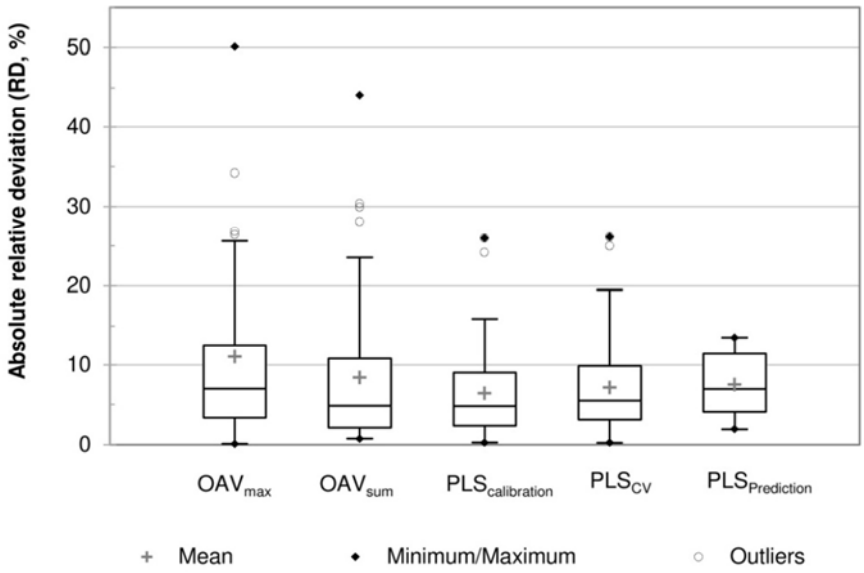


Fig. 6. Percentage of absolute relative deviation (RDs, %) for odor concentrations (OC in OU_E m^{-3}) predictions standing outside of the 95% confidence interval for the OC measurements. Predictions were conducted by a partial least squares (PLS) regression model with three components and odor surrogates such as the maximum odor activity value (OAV_{max}) and the sum of individual OAV (OAV_{sum}). The RDs from the PLS calibration model, cross-validation (CV) and test set validation (prediction) are depicted

Odor concentrations predicted throughout PLS model calibration (PLS_{CAL}) and validation (PLS_{CV} and PLS_{pred}) displayed similar RDs distributions (Fig.6), thus demonstrating the model robustness and reliability when predicting OC in new gas samples collected under similar pilot conditions. These validation processes examined the predictive ability of the model at pilot scale; however, its final applicability must be assessed by using gas samples from real scale composting facilities, preferably upon composting of organic matrices not included in the present research work. One reason for enlarging this validation process is that volatile compounds and odor emissions can considerably differ during aerobic treatment as a function of the process conditions (i.e., aeration rate, moisture, porosity) and substrates compositions (Blazy et al., 2014). Parker et al. (2012) emphasized the importance of validating statistical odor models with different datasets for determining their general limitations and advantages.

Despite the substantial variation in terms of experimental conditions, OC was successfully predicted by OAV during composting of solid wastes and digestates at pilots scale. These encouraging results provide a basis to support the use of OAV in odor monitoring at larger scales. To achieve this ultimate goal, ODT dataset in compliance with the EN 13725 must be broadened to guarantee that the input data for OC prediction model accounts for the entire components present in the gas matrices (Wu et al., 2017). Similarly, more accurate OC and chemical concentration values from composting gas exhausts are required to reflect the real composition of the odorous gases and avoid underestimation of OAV values through gas sampling storage. On-line sensory and analytical measurements have been reported as

promising methods to overcome this shortcoming (Hansen et al., 2016; Muñoz et al., 2010). New standardization strategies are also necessary to reduce the variability in responses from the odor panel during OC measurements since they are the reference values to establish predictive odor models. Hence, implementing different calibration criteria, such as selecting panelists based on other standards besides n-butanol, should be further studied.

4. Conclusions

Gas exhausts from the active composting phase of solid wastes and digestates were analyzed through dynamic olfactometry and analytical methods. By applying an odor activity value (OAV) approach based on odor detection thresholds (ODT), 22 key odorants were quantified and correlated with odor concentration (OU_E m^{-3}). Partial least squares (PLS) regressions and simple linear regressions with two OC surrogates (OAV_{max} and OAV_{sum}) were tested to search for the best sensory measurement predictions.

OAV_{max} and OAV_{sum} provide overall insight into OC trend along the active composting phase (R^2: 0.67-0.73) with a certain level of uncertainty. Hence, a PLS model consisting of the weighted OAV from 10 odorants enabled to enhance OC predictions. The PLS regression model explained from 74% to 76% of the OC variance throughout cross-validation and test set validation. Moreover, OC values regressed by this multivariate model were less underestimated (7%) than those predicted by OAV_{max} and OAV_{sum} (11-13%). The PLS model's robustness was also demonstrated by the low absolute relative deviations (RD) of OC predictions in regards to the 95% interval confidence boundaries (RD= 0.2-26%). Enlarging the validation process with new test sets is required to prove the applicability of the developed PLS model for other process conditions.

The applied OAV_{max} and PLS regressions analysis highlighted the relevance of hydrogen sulfide, methanethiol, dimethyl sulfide, and dimethyl disulfide as odor pollution sources during the aerobic treatment of solid wastes and digestates. 3-methyl butanol and ethanol showed a negative link with OC in the developed PLS model; yet, the relationship between these odorants and possible antagonistic effects on odor perception must be explored in future sensory experiments.

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Supplementary material 1

Section 1S. Recovery rates of main odorants detected upon composting of solid wastes and digestates

The recovery rates of the main odorant detected upon composting were determined for two different gas sampling system. For volatile organic compounds (VOC), gas samples were collected into 30 L nalophan bags, then adsorbed into carbotraps (Carbotraps 349, Perkin Elmer, USA), and consequently analyzed in a TD/CG-MS by external calibration. In order to evaluate the recovery rates for the principal VOC, gas mixtures of VOC were prepared by spiking a known volume of liquid chemical standards (Purity > 98%, suppliers: Fluka, Fisher, Janssen Chemica, Sigma Aldrich, Across Organic and Alfa Aesar) into 20 mL glass vials sealed with Teflon-lined silicone septum. Two hours after injection and volatilization at room temperature, two mL of the headspace was injected into nalophan bags containing 30 L of dry air with a gas-tight syringe (SGE, Australia). The initial concentration (0 h) of the prepared gas mixture was quantified by external calibration with the GC/MS (Table 1S). After that, the concentration of VOC was evaluated after 3 and 6 hours of storage at room conditions by sampling the gas mixture onto sorbent tubes at a mean flow rate of 53.2 mL min^{-1} for around 5 min and then analyzing the carbotraps with the TD/GC-MS. Compounds quantification was conducted by external calibration ($r > 0.99$). The recovery rate of the entire sampling system (nalophan bag, tubes, and carbotraps) was evaluated based on the initial gas mixture concentration and expressed on a percentage basis as shown in Table 1S.

For volatile sulfur compounds (VSC), gas samples collected in the nalophan bags were directly pumped toward a loop injection valve present in the GC coupled to electrochemical detection (MEDOR). To assess the recovery rates of five VSC (table 1S), an initial gas mixture was prepared by injecting a known volume of liquid (>98.5 %; Sigma-Aldrich and Across Organics) and gas standards (201 ± 10 ppm and 207 ± 10 ppm; H_2S and CH_3SH gas cylinders, Air Liquid) into a nalophan bag containing 30 L of analytical grade air. The initial gas mixture concentration was measured by external calibration with MEDOR ($r > 0.99$) and compared with VSC levels upon three and six hours of gas sample storage to yield VSC recoveries (Table 1S). Recovery rates in nalophan bags for trimethylamine, ammonia, propanoic acid, ethyl acetate, and dimethyl trisulfide were not measured in this study and then consulted in the literature as shown in Table 1S.

Table 1S. Recovery rates (%) of principal VOC and VSC for the used gas sampling systems at 3 and 6 hours of storage time in nalophan bags

Odorant	Initial concentration on the gas mixture (µg m^{-3})	Recovery rates (%) at different storage times in nalophan bags		Reference
		3 hours	6 hours	
Acetic acid	406	77,6	63,1	-
Methanol	1825	109,1	90,7	-
2-Butanol	2614	64,4	58,0	-
Ethanol	1468	117,3	95,4	-
3-Methyl-1-Butanol	19.5	52,5	61,5	-
Acetone	3303	65,2	89,1	-
2-butanone	1828	91,3	73,0	-
2.3-butanedione	379	85,6	74,1	-
Carbon disulfide	5693	83,7	78,7	-
Alpha-pinene	257.3	94,5	58,1	-
Beta-pinene	92.1	42,3	58,9	-
Limonene	72	105,1	105,0	-
Ethanethiol	969	101,5	103,0	-
Methanethiol	1334	105,0	103,0	-
Hydrogen sulfide	1165	102,4	108,5	-
Dimethyl sulfide	666	103,0	105,1	-
Dimethyl disulfide	1428	109,0	110,8	-
Ammonia§	-	93,8	84,7	(Sironi et al., 2014)
Propanoic acid§	-	74 (4-24 h)		(Hansen et al., 2012)
Trimethylamine§	-	81 (4-24 h)		(Hansen et al., 2012)
Ethyl acetate§	-	90 (2-4 h)		(Van Durme and Werbrouck, 2015)
Dimethyl trisulfide§		90 (6h)		(Le et al., 2013)

§Recovery rates reported in the literature. In parentheses the storage time in nalophan bags before analysis.

Section 2S. Recoveries of two VSC during dilution with a gas-tight syringe

The recovery rates of H_2S and CH_3SH was investigated by injecting 100 mL of gas standards (Table 2S) into a nalophan gas bag containing 30L of dry air. The gas-tight syringe employed to perform dilution accounted for a volume capacity of 100 mL (SGE, Australia). Once injected, the nalophan bag was immediately analyzed through a GC coupled to electrochemical detection. The final gas bag concentration was measured through external calibration ($r>0.99$) and compared with the theoretical concentration to compute the recovery rate of both VSC.

Table 2S. Effect of the gas-tight syringe on VSC recoveries after dilution and injection in nalophan bags

Compound	Gas cylinder concentration	Theoretical concentration with a dilution factor of 300 (mg m^{-3})	Measured concentration (mg m^{-3})	Recovery rates (%)
Hydrogen sulfide	201±7 ppm	0.95	1.14	120.9
			1.17	124.1
Methanethiol	207±10 ppm	1.38	1.34	97.0
			1.33	96.2
Mean				109 ± 15

Table 3S. Odor detection thresholds (ODT) measured by dynamic olfactometry

Compound	Initial gas bag concentration (mg m^{-3})	Number of replicates	Relative losses (%) for storage in nalophan bags	Exposure concentration (mg m^{-3})	Measured ODT (mg m^{-3})
Hydrogen sulfide	1.47-0.37	5	~0	1.47-0.37	0.00047
Limonene	280.7	3	~0	280.7	0.183
Acetic acid	104.9	3	22.4	81.40	0.019
Trimethylamine	1.24	3	18.7[a]	1.01	0.00073
Methanethiol	1.05	3	~0	1.05	0.00021
Dimethyl disulfide	70.8	3	~0	70.8	0.00980
Dimethyl sulfide	56.4	3	~0	56.4	0.00690
P-cymene	200.7	3	-	200.7	0.12
Ethanethiol	0.51	3	~0	0.51	0.00022
Ammonia	267	3	6.1[b]	250.7	1.81
2,3-butanedione	2.97	2	14.4	2.5	0.0003
Carbon disulfide	211	2	16.3	176.6	0.49
Beta pinene	404.3	3	57.7	171.0	0.28
3-Methyl butanol	107.6	3	47.5	56.5	0.026
Alpha pinene	400.4	2	5.5	378.4	0.22

As reported by [a]Hansen et al., 2012 (storage time: 4-24 h) and [b]Sironi et al., 2014 (storage time: 3h).

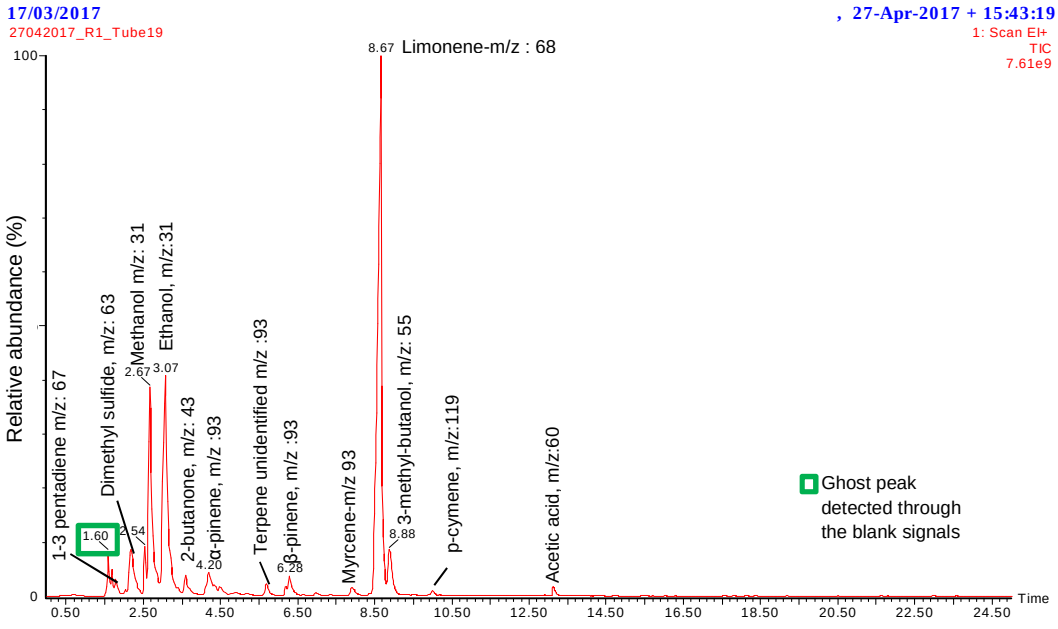


Fig. 1S. GC chromatogram for a gas sample collected during composting of household biowaste

Supplementary materials 2, 3 and 4

The datasets of compounds' concentrations levels and odor concentrations (Supplementary material 2), OAV (Supplementary material 3) and the training and test sets used to develop the PLS models (Supplementary material 4) are published online on the following link: https://doi.org/10.1016/j.atmosenv.2018.12.030

Supplementary material 5. Odor emission profiles during composting process of solid wastes and digestates: Odor concentration in OU_E m^{-3} and OAV (dimensionless)

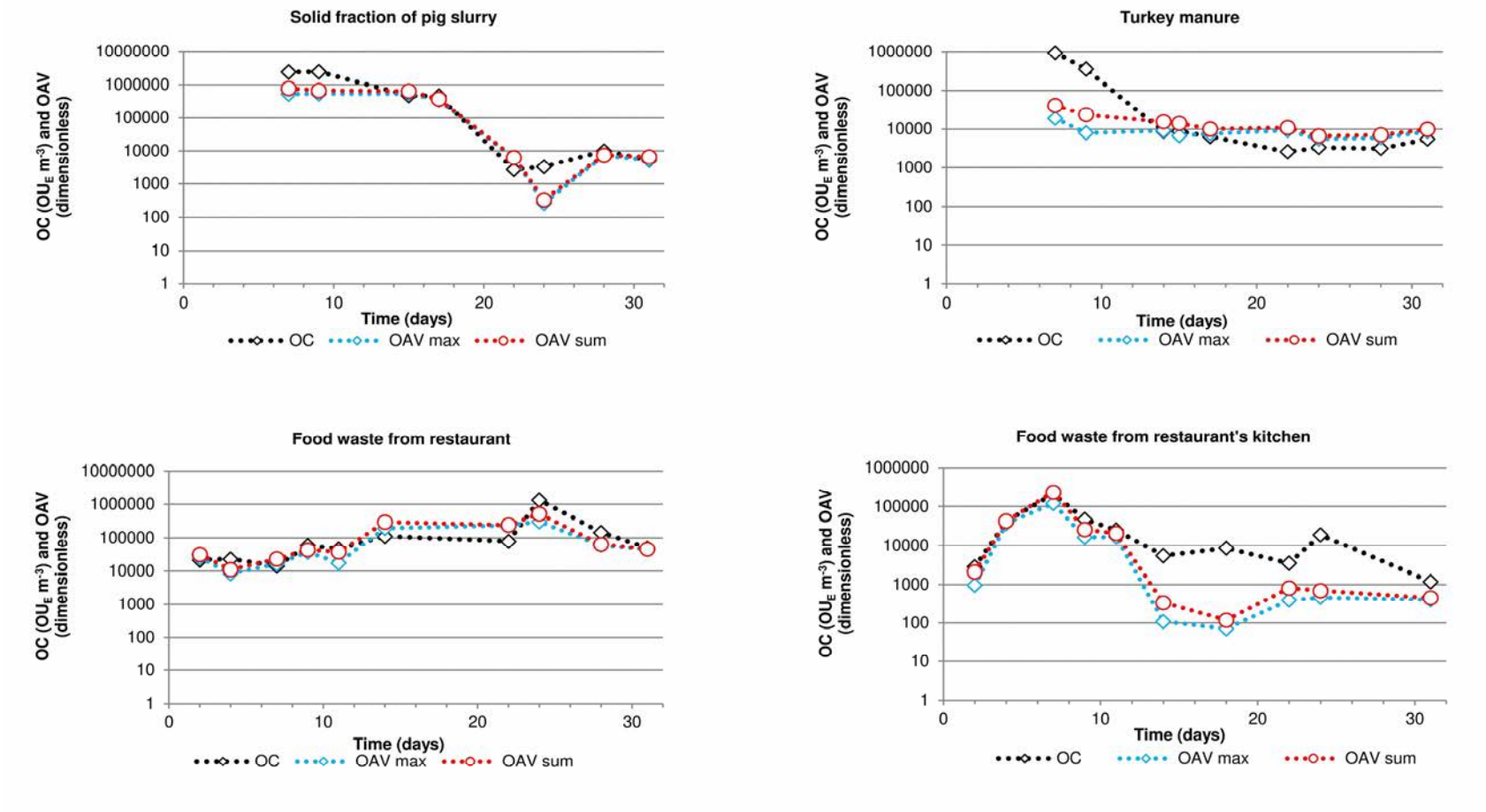


Fig. 2S. Odor emission profiles during composting process of solid wastes and digestates: Odor concentration in OU_E m^{-3} and OAV (dimensionless)

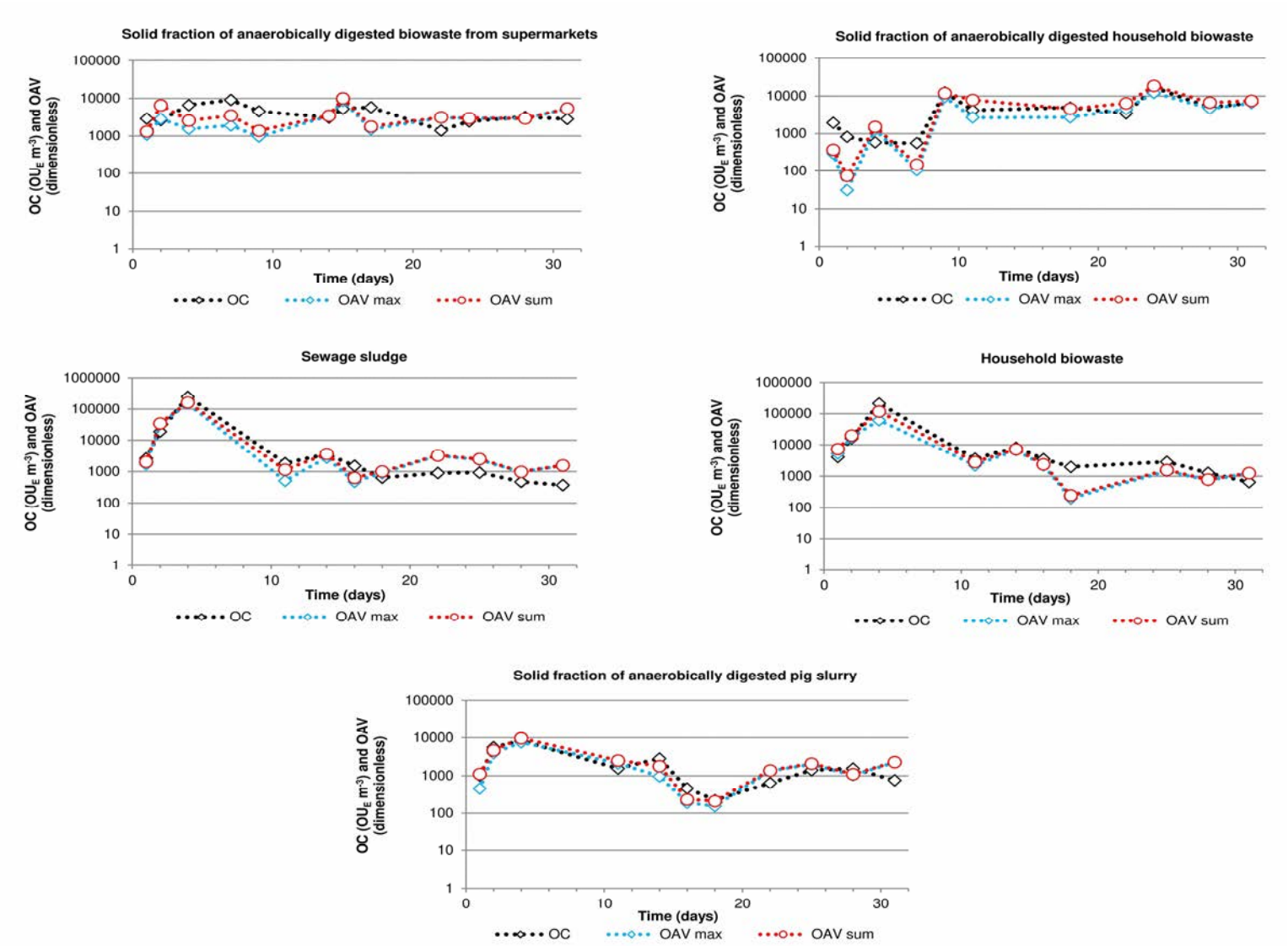


Fig. 2S. Odor emission profiles during composting process of solid wastes and digestates: Odor concentration in OU_E m^{-3} and OAV (dimensionless)

Supplementary material 6.

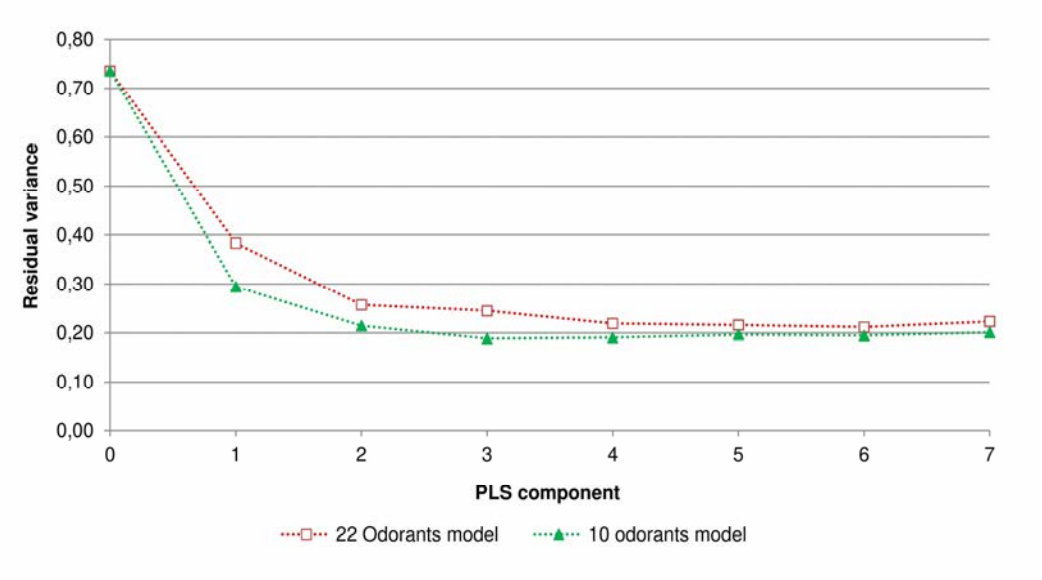


Fig. 3S. Changes in residual variance depending on the components number to developed two PLS models. The three-components PLS models exhibited the lowest residual variance

References Supplementary material

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Conclusions and perspectives

Nowadays, odor and air pollution control have become a crucial point on the agenda of environmental regulatory policies and waste management plans. The composting process is associated with the release of hazardous and odorous gas emissions that have a negative impact on the environment and human health. Among the multiple issues arising from gas emissions in the waste bio-processing industry, odor nuisance generation is undeniably one of the principal challenges. Malodors remain the main cause of complaints brought against the waste process units, probably because they are the most perceivable way of air pollution and the ones that affect more directly the comfort and wellness of neighbors and plant workers. This severe issue has caused strong public opposition to this industrial activity, finally leading to legal lawsuits and the closure of waste treatment facilities.

Notably, the characterization of odor emitting sources constitutes the first step and foundation to seek for suitable odor abatement strategies (either by preventive measures or end-of-the-pipe technologies) that can reverse the environmental and odor impact linked to the waste processing. Odor monitoring generally involves the measurement of the odor stimuli by sensory techniques and the identification and quantification of the odor-causing compounds evoking the physiological response through analytical methods. Despite the relevance of a complete odor assessment in air pollution control, the literature review performed in **Chapter 1** put in evidence a clear limitation on the number of odor and chemical emission inventories for the composting process of solid wastes and residual organic products (ROP). Overall, three principal axes of arising issues were highlighted throughout this bibliographic analysis: i) the odor impact of some operational stages of the composing process (i.e., turning, storage, sieving, shredding, and curing) have been scarcely addressed in the literature, which difficult the evaluation of the real odor and environmental impact of the entire process; ii) Most of the research works evaluating odor emissions during the composting process of different organic substrates have been conducted in unstandardized conditions (i.e., industrial scale, disparate methodology), leading to a large variation on published results. Hence, the study of odors upon composting lacks a systematic characterization that hinders the inter-comparison among studies and organic matrices composted; iii) There is an urgent need to ease and assist odor surveys in waste treatment units by finding easily acquired and costs-effective instrumental-based measurements that serve as estimators or predictors for the expensive and complex sensory measurements.

In response to the manifested gaps of knowledge, this thesis had two-fold objectives: i) to characterize the chemical and odor composition of gas emissions released during the composting process of solid wastes and digestates, and ii) to provide new insight into the relationship between the chemical composition of gas emissions and odor concentration.

The first experimental part of this manuscript (**Chapter 3**) was addressed toward the acquisition of odor and chemical emissions inventories for different operational stages of the composting process, as well as the assessment of the odor impact and odor generation patterns when performing this biological

treatment. To this end, the storage, the aerobic treatment by forced aeration (active phase), the turning and curing process of anaerobically digested sewage sludge (ADS) were simulated at pilot scale. The gas emissions released during each operational stages were extensively monitored via dynamic olfactometry and analytical methods (i.e., TD-GC/MS, acid traps and MEDOR) to quantify the odor concentration (OC), volatile organic compound (VOC), volatile sulfur compound (VSC), ammonia. OC was also related to the pilots' outflows to provide the odor emissions rates (OER in $OU_E\ h^{-1}\ kgOM_0$). Contrarily, chemical concentrations were weighted against measured and reported odor detection thresholds (ODT) to assess the odor potential of the volatile compounds composing the gas exhaust through the odor activity value (OAV) approach.

A total of 19 compounds were identified and quantified throughout the different stages of ADS composting. Notably, the total mass emitted along the entire process was principally attributed to ammonia (55.5%) and VSC (20.6%) such as dimethyl disulfide, H_2S, dimethyl sulfide, and methanethiol. From all operational steps studied, the storage and active phase of ADS were the primary sources for air pollution by accounting for 16% and 77% of the total cumulative mass emitted (35 mg kg^{-1}ADS). It is worth mentioning that the first eight days of the active composting phase, called "the earlier active phase", were responsible for 40% of the total mass of volatile compounds released during composting simulation.

Based on the OER assessment, the storage, the earlier active phase and the first turning were considered as crucial stages for odor emissions. OER increased in a factor 10 during ADS storage, reaching a maximum value of 17.6 $OU_E\ h^{-1}\ kg^{-1}$ADS. Once aerobic conditions were set, a first OER peak of 56.6 $OU_E\ h^{-1}\ kg^{-1}$ADS was observed within the first days of the active phase as a result of the rise on microbial activity, temperature and gas stripping. Nevertheless, the most intense OER peak was detected when conducting the first turning of the compostable mixture (317 $OU_E\ h^{-1}\ kg^{-1}$ADS). During the turning process, the compostable material is loosened and the solid media, including the biofilm particles, are more exposed to the gas phase. Finally, OER values dropped (0.18-12.6 $OU_E\ h^{-1}\ kg^{-1}$ADS) for the middle and later active composting phase, the second turning and curing stage as a result of the substrate stabilization.

The results from OEF assessment also underlined the relevance of active composting phase (82%), storage (5%), and first turning (5%) in odor generation with some particular differences. For instance, the turning process was the cause of punctual and strong odor episodes occurring in a short lapse of time (2 hours), confirmed by an OEF per stage duration of 295 $OU_E\ h^{-1}\ kg^{-1}$ADS. In contrast, the active phase was responsible for lower but constant odorous emissions released in several days, particularly at the beginning of the aerobic treatment (40.5 $OU_E\ h^{-1}\ kg^{-1}$ADS).

The OAV approach enabled to identify the main drivers of odor nuisances, as well as provide some notions about the emissions' odor quality for the diverse operational stages of ADS composting. In

general, VSC and acetic acid were the leading odorants. Nevertheless, when looking deeply, it was evidenced a shift in the odorant composition as the biological treatment of ADS proceeded. For example, dimethyl disulfide (DMDS), dimethyl sulfide (DMS), and methanethiol were the predominant odorants for the first composting stages such as storage, early active phase and, first turning. These substances are easily recognized because they exert rotten-cabbage and garlic -like odor experiences that can provide preventive warns to composting practitioners about the release of odor plumes. Contrarily, the further stages of ADS's composting (i.e., the end of the active phase, second turning and maturation) were principally governed by H_2S emissions and a possible perception of rotten egg-like odors.

A principal component analysis (PCA) explaining 77 % of the variability in OC and OAV dataset allowed the visualization of gas samples' clusters according to the process stage in which they were taken. These samples groups were successfully associated with the main odor-causing compounds determined via OAV, thus facilitating the recognition of odor patterns upon ADS composting. PCA could therefore constitute a powerful tool in odor survey programs for waste treatment sites.

The research work performed in **Chapter 3** opened the gate to new areas of future research. Some remarkable recommendations and perspectives derived from this first experiment are:

- It is of great interest to extend and validated the conclusions obtained through the odor impact assessment of digestate composting to the biological treatment of other solid wastes. Therefore, the odor emissions patterns throughout different composting operational stages of solid wastes and raw substrates should be assessed and compared with the obtained results. The OER trend obtained during the aerobic treatment of ADS was rather similar to the ones reported for the forced aeration treatment of some solid wastes (i.e., municipal solid waste and sewage sludge); however, the similarities and variations on odor emissions between both type of substrates could not be established for other composting operations namely, turning and curing, due to the lack of emissions inventories reported in the literature.

- In our study, the odor impact assessment of ADS composting was limited to the evaluation of four operational stages. Other relevant process steps, such as sieving of the compostable mixture, storage of final compost, solid-liquid separation, and digestate spreading should be similarly simulated and monitored to obtain a wider view of the generation of odor nuisances through the entire process. To this end, new experimental devices must be designed and set-up to simulate this process steps under controlled laboratory conditions. This type of simulation can represent a challenge for certain stages (i.e., spreading and sieving) as they involve the gas sampling of diffused emissions while conducting the waste handling and movement. One possible option to collect this sort of area or volume emissions sources would be to adapt wind tunnels or flux chambers (i.e., using the "lung principle") to

account for stable flux conditions and defined sweep air flows while performing these operations in an enclosed room.

The pivotal role of the active phase in odor and air pollution generation was highlighted along the aerobic treatment of ADS (**Chapter 3**). In line with these first results, the state of the art on odor emissions from composting showed a marked preference of studies for assessing odorous gas emissions from the composting active phase of organic matrices because it is generally regarded as the principal stage driving to odor nuisances. Accordingly, the research work carried out in **Chapter 4** was focused on characterizing extensively the chemical and odor composition of gas emissions released during the forced aerobic treatment of solid waste and digestates under controlled pilot-scale conditions. For this purpose, ten solid wastes and five digestates were composted in pilot-scale reactors of 300 L that were supplied with positive forced aeration for approximately 30 days. The resulting gas exhausts were thoroughly analyzed to yield the cumulative mass emitted and the chemical profiles of VOC, VSC, and ammonia. Likewise, gas samples were assessed by dynamic olfactometry to measure OC, OER, and OEF. The chemical contribution of the emitted compounds was then obtained on a percentage basis (PC_i, %) by dividing the cumulative mass production of a specific compound by the net cumulative mass.

A total of 60 compounds were identified all along the composting experiments. These substances belonged to nine chemical categories, namely, sulfur compounds, terpenes, ketones, alcohols, alkenes, nitrogen compounds, aromatics hydrocarbons, acids, and esters. The types of molecules detected in the gas exhaust from composting were directly associated with the nature of the substrates composted. Indeed, the results showed that organic matrices containing fruits, vegetables, leaves, brush, and food waste such as biowastes, household wastes, and green wastes, generated gas emissions rich in terpenes and oxygenated compounds (i.e., alcohols, acids, esters, and ketones) with PC_i fluctuating between 21-90 % and 9-71%, respectively. Terpenes emissions were also linked to the lignocellulosic material used as a bulking agent. Others solid wastes and ROP that present low carbon to nitrogen ratios such as agricultural wastes (turkey manure and solid fraction of pig slurry), sewage sludge, and some digestates caused large ammonia emissions (PC_i= 57-93%) when they were treated aerobically.

In **Chapter 4**, special attention was paid to the evaluation of the OER and OEF in composting as a response to the lack of odor emission inventories observed in the literature. The results indicated that solid wastes and digestates followed similar OER profiles that were marked by an increase of OER during the first 15 days of the aerobic process. This rise in OER values coincided with the thermophilic phase in which most of the readily available organic matter is broken down by microorganisms. The maximum OER for the studied solid wastes ranged from 829 to 27306 $OU_E\ h^{-1}\ kg^{-1}OM_0$, whereas digestates exhibited maximum OER that fluctuated from 22 to 115 $OU_E\ h^{-1}\ kg^{-1}OM_0$. Finally, OER tended to drop by the end of the process when the microbial activity slowed down.

The composting process of solid wastes showed more substantial OEF ranging from 3089 to 65 OU_E $g^{-1}OM_0$, while the aerobic post-treatment of digestates exhibited meager OEF varying from 30.5 to 8.6 OU_E $g^{-1}OM_0$. This difference between OEF was associated with the fact that digestates were previously stabilized by the anaerobic digestion process, thus reducing their emission potentials of odorants throughout the aerobic degradation. Also, digestates were typically composted with wood chips that decreased the amount of readily degradable organic matter present in the compostable mixture and anaerobic zones.

The highest OAV (OAV_{max}) along the entire process were traced because they provided valuable information about the odorants contributing the most to odor nuisance. Then, the OAV_{max} for each quantified substance was weighted by the sum of all determined OAV_{max} ($SOAV_{max}$) to yield the percentage of odor contribution (PO_i,%). In general, VSC were the major odor contributors (PO_i= 54-99%) for all composted substrates. The huge odorous potential of these substances is associated with their high volatility, extremely low ODT and thus significant capability to create odor sensory stimulus even at reduced concentrations. The main VSC contributing to odor nuisances were methanethiol, ethanethiol, and H_2S as they represented from 34% up to 95% of the total $SOAV_{max}$. According to our results, methanethiol was the main odorant for 73% of the composting simulation experiments. Notably, odor mitigation strategies could be better implemented and designed by taking into account these identified odorous compounds. Moreover, reducing the number of target compounds can enhance the efficiency and reduce the costs of odor monitoring programs.

The following recommendations and perspectives arose from the acquired results and experiments performed in **Chapter 4**:

- The reduction of the odor nuisances through the application of a prior anaerobic digestion step before composting organic substrates were emphasized in **Chapter 4**. The OEF of some digestaste were drastically lower than the ones acquired for the raw substrates derived from the same type of feedstock. These results pointed out the evident gains of coupling anaerobic digestion to composting process in terms of odor management, energy production, and generation of safer soils amendments.

- Co-composting of organic substrates presenting different biodegradabilities constitutes not only an appealing alternative to improve the process' performance in terms of sanitization and drying of the treated wastes but also a strategy to reduce the odor nuisance potential of the aerobic treatment. This was confirmed through the composting process of municipal solid waste (MSW) with green wastes in **Chapter 4**. More efforts should be thus devoted to assessing the suitability of co-composting wastes with high odor emission potential (i.e., MSW, sewage sludge, agricultural wastes) and matrices exhibiting lower biodegradability (i.e., digestates) as an odor prevention strategy.

- Further efforts should be similarly addressed toward the determination of OEF of diverse organic substrates and mixtures of substrates at industrial and laboratory scale. The creation of an online database of OEF for composting and methanization process would assist practitioners and researchers in assessing odor impact along these biological treatments.

- The harmonization of ODT values remains a real challenge in odor sciences because of the large variability of odor sensitivity from assessors and differences in the methodological approach to evaluate them. More research studies are needed to enlarge the list of volatile compounds' ODT by following the guidelines of standardized methods such as the EN 13725 and ASTM 679. Some strategies could be adopted to tackle the variability on ODT: i) to test new reference materials (besides n-butanol) via novel standardization protocols that offer a broader view of odor sensitivity of panelists who evaluate the ODT of pure substances; ii) create an active online network and database of ODT measurements that promote the traceability and comparability of results among different laboratories on-real time.

The last chapter of this manuscript (**Chapter 5**) was devoted to analyzing the feasibility of instrumental-based measurements (odor activity values) to predict the odor concentration (OC) of emissions released throughout the aerobic treatment of different organic matrices. Although the correlation between OC and OAV has been formerly proved for the composting process, the developed prediction models has been validated with one substrate and the use of powerful multivariate analysis have not been taken into account. Hence, we analyzed the gas emissions released through the forced aeration treatment of six solid wastes and three digestates in 300 L pilots for approximately 30 days. A total of 92 gas samples were collected and analyzed by TD-GC/MS, MEDOR, acid traps, and dynamic olfactometry to quantify the VOC, VSC, NH_3, and OC, respectively. Once the chemical concentrations of compounds were computed, their OAV were obtained using measured and reported ODT. The feasibility of OAV to predict OC was then assessed through simple linear regression models and partial least squares (PLS) regressions after scaling both variables via Log-transformations. Two odor surrogates derived from OAV calculation were employed to perform the simple linear regression: OAV_{max} (the highest OAV value) and OAV_{sum} (the sum of all OAV of compounds present in the gas sample).

A total of 22 quantified volatile compounds showed concentrations that exceeded at least once their ODT and yielded OAV superior to one. VSC were the major odor contributors, accounting for 89% of the odorants exhibiting OAV_{max} during aerobic treatment of solid wastes and digestates. Moreover, OAV_{max} enabled to explain 67% of the measured OC variance ($p<0.0001$) and yielded a function Log (OAV_{max})= 0.93 Log (OC), which was relatively close to the 95% confidence interval. In the case of OAV_{sum}, the goodness of fit of linear function Log (OAV_{sum})= 0.97 Log (OC) was slightly better than for

OAV_{max} (R^2: 0.73, $p<0.0001$). However, both explanatory variables led to underestimate OC values for 63% of the analyzed gas samples. For instance, OC predicted by OAV_{sum} and OAV_{max} were on average 11-13 % inferior to the measured OC. The moderately strong linear correlation (R^2= 0.67-0.73%, $p<0.0001$) obtained between these odor surrogates and OC suggested that they can provide a preliminary estimation of odor nuisances during composting of solid waste and digestates with an expected level of uncertainty.

A PLS model including ten odorants was capable to explain 74% of the OC variance upon cross-validation and 76% of the OC variance through test set validation. According to PLS regression analysis, VSC were strongly correlated to OC and showed one of the highest regression coefficients (H_2S, CH_3SH, and DMDS), thus confirming the results obtained through OAV_{max}. However, 50% of OC values predicted through the PLS model were also underestimated when compared with the measured OC of the gas samples. These predictions were on average 7% inferior to the measured or observed OC. This means that the developed PLS model enabled to predict better the measured OC with less average underestimation than OAV_{max} (13%) and OAV_{sum} (11%). Similarly, the results showed that OC predictions yielded by the PLS model were less dispersed around the boundaries of the 95% interval confidence than the ones obtained by the odor surrogates. For instance, the absolute relative deviation (RD, %) of predicted values standing outside the 95% confidence interval through the PLS fluctuated from 0.2% to 26%, whereas the odor surrogates (OAV_{max} and OAV_{sum}) generated OC predictions with RD ranging from 0.7% up to 50%.

Based on the acquired results in **Chapter 5**, the perspective and recommendations to improve and validate the developed models for OC prediction via OAV are:

- For certain molecules, compounds losses were observed during the storage of gas samples in nalophan bags. The EN 13725 recommends to carry out gas sampling in bags made of different materials, including polyethyleneterephthalate (nalophan), polytetrafluoroethylene, among others. Although their use is advised by the norms, these types of gas sampling devices are subjected to a certain extent to compounds losses through chemical reaction and adsorption. To tackle this problem, the evaluation of volatile compounds recoveries during storage in nalophan bags must be enlarged. It is also necessary to establish comparisons within the chemical fingerprints of gas emissions analyzed with and without this gas sampling step. Nevertheless, gas sampling in bags to conduct delayed dynamic olfactometry remains a necessary step in the practice (at both industrial and laboratory scale) since on-line or direct dynamic olfactometry is difficult to implement and expensive. The use of double nalophan gas bags accounting for a double layer separated by a void space (filled with nitrogen or air) is currently profiled as a good alternative to reduce compounds losses during gas sampling.

- It should be highlighted that the applicability of the developed PLS model for other process conditions must be explored by enlarging the validation process with new test sets. The next step would be therefore to assess the feasibility of the constructed models in predicting OC for gas samples collected at industrial scale or throughout the aerobic treatment of organic matrices not considered in this study. Similarly, the suitability of the developed models to predict OC on real scenarios should be examined by linking them to odor dispersion models.

- OC predictions via OAV constitute only a first step in the determination of odor nuisances in composting plants. Hence, further efforts should be addressed toward the correlation of the chemical composition and OC to other qualitative odor dimensions such as hedonic tone, odor quality, and odor intensity. To establish these correlations, the OC evaluation and chemical analysis could be experimentally coupled to the measurement of hedonic tone and odor quality.

UNIVERSITE MATIERE BRETAGNE MOLECULES LOIRE ET MATERIAUX

UNIVERSITÉ DE RENNES 1

Titre : **Caractérisation des émissions gazeuses et des odeurs en compostage. Etude de la corrélation entre la concentration d'odeur et la composition chimique des émissions**

Mots clés: nuisance olfactive, compostage, analyses chimiques, concentration d'odeur, analyses sensoriel

Résume: La valorisation des déchets par le compostage et la méthanisation est encouragée par les politiques de l'UE. Cependant, ces technologies de recyclage des déchets sont confrontées à un défi crucial en matière de libération et de contrôle des émissions de gaz odorants. En effet, la pollution par les odeurs est la principale cause d'opposition du public au traitement des déchets, ce qui a entraîné la fermeture et des poursuites en justice pour les unités de traitement des déchets. À l'heure actuelle, les inventaires des émissions d'odeurs et de produits chimiques pour appuyer les plans de gestion des odeurs et de la pollution atmosphérique font défaut, en raison de la complexité des évaluations des odeurs, impliquant généralement des analyses sensorielles et chimiques. L'objectif de cette thèse était donc de caractériser de manière détaillée les émissions de gaz et les odeurs lors du processus de compostage. À cette fin, les émissions d'odeurs et de polluants ont tout d'abord été étudiées au cours des différentes étapes opérationnelles du processus de compostage, à savoir le stockage, la phase active, le retournement et la maturation. Les résultats ont montré que la phase active et le retournement jouent un rôle essentiel dans les générations de nuisances olfactives causées principalement par les composés soufrés volatils (CSV). Des efforts supplémentaires ont ensuite été consacrés à la caractérisation des émissions de gaz au cours de la phase active de compostage de quinze déchets solides et du digestat, permettant ainsi de corroborer l'importance des CSV sur la production d'odeurs lors du compostage et de différencier l'impact des émissions de gaz sur les odeurs en fonction des matières premières des déchets. La dernière partie de ce travail de recherche a été consacrée à la corrélation des mesures sensorielles et chimiques, par le biais de méthodes de régression simple et multiple visant à faciliter et à renforcer le contrôle des odeurs dans les unités de traitement des déchets. Notamment, un modèle des moindres carrés partiels améliore la prévision de la concentration d'odeurs grâce à la composition chimique des gaz émis.

Title: **Characterization of gas emissions and odors upon composting. Study of the correlation between the odor concentration and chemical composition**

Keywords: odor nuisance, composting process, chemical analysis, odor concentration, sensory analysis

Abstract: Waste valorization through composting and methanization are actively promoted by the EU policies. However, these waste recycling technologies face a crucial challenge regarding the release and control of odorous and hazardous gas emissions. Indeed, odor pollution is the principal cause for public opposition to waste processing, leading to the closure and lawsuits for waste treatment units. Currently, there is a lack of odor and chemical emissions inventories to support odor and air pollution management plans due to the complexity of odor assessments, generally involving sensory and chemical analysis. Hence, the aim of this PhD thesis was to characterize extensively the gas emissions and odors released during the composting process. To this end, the patterns of odor and pollutant emissions were first traced throughout different operational stage of composting process, namely, storage, active phase, turning and curing. The results showed that the active phase and turning played a pivotal role in odor nuisance generations which were mainly caused by volatile sulfur compounds (VSC). Then, further efforts were focused on characterizing the gas emissions released along the composting active phase of fifteen solid wastes and digestate. The results corroborated the relevance of VSC on odors production during composting and enabled to differentiate the odor impact of gas emissions as a function of the wastes' feedstock. The last part of this research work was devoted to correlate both, sensory and chemical measurements, through univariate and multivariate regression analysis to ease and strength odor monitoring in waste treatment units. Notably, a partial least squares model improved odor concentration prediction based on the chemical composition of emitted gases.