MINERALOGIE ET GEOCHIMIE DU MATERIEL PARTICULAIRE RESPIRABLE (PM10 et PM2.5) PRESENT DANS L'AIR DE SANTIAGO, CHILI; contribution à sa caractérisation et l'identification de ses sources.

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MINERALOGIE ET GEOCHIMIE DU MATERIEL PARTICULAIRE RESPIRABLE (PM10 et PM2.5) PRESENT DANS L'AIR DE SANTIAGO, CHILI;
contribution à sa caractérisation et l'identification de ses sources.

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Je dédie cette thèse à ma Maman, Silvia Durán,
qui m’a encouragé jusqu’à la fin.

No se vive celebrando victorias, sino superando derrotas.

(El Ché)

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Ana Valdés

RESUME

Cette thèse présente la caractérisation géochimique du matérielle particulaire de l'air respirable (PM10 et PM2.5) du Santiago du Chili. L'objective principal de l'étude, est l'identification des sources polluantes à travers des traçages d'éléments chimiques afin d'identifier leur origine et les processus de génération principaux. Ceci passe par l'analyse des concentrations en éléments majeurs et traces, leurs variations entre sites, saisonnières et interannuelles. Il s'agit d'un pré-requis pour aborder l'impact de ces polluants en terme de santé publique, et fournir des outils pour faire évoluer les politiques publiques.

Ce présent travail, a permis aussi, de quantifier les niveaux et variations des concentrations en éléments chimiques potentiellement toxiques qui peuvent impacter sur le taux de mortalité liées à pathologies cardiaques ou respiratoires.

Mot clés : Géochimie, pollution, air, sources, matériel particulaire (PM10, PM2.5), santé publique.

ABSTRACT

This thesis is a geochemical characterization of breathable particulate matter (PM10 et PM2.5) in Santiago, Chile. The principal objective is the identification sources trhough of determination of tracers elements origins and genesis process. Major and traces elements has been analyzed in terms of the variation concentrations between different sites, seasonality and years. The chemical characterization of some elements is necessary in order to understand the impact on the human health and improve the quality of air according with public politics. Therefore, this works also allows to quantified concentrations level of some potential toxic elements that could be impact on the mortality range of cardiac and respiratory illness.

Keys words: Geochemistry, pollution, air, sources, MP10, MP2.5, Human Health.

TABLE DE MATIERES

PRESENTATION DU MANUSCRIT

Structure du Manuscrit

Le manuscrit est divisé en six parties présentées sous forme de chapitres, de publications et d'articles en cours de préparation.

L'*introduction* présente la problématique centrale du cadre d'étude : la pollution urbaine et les principaux polluants existants dans l'atmosphère comme les polluants gazeux (oxydes d'azote, oxydants photochimiques, hydrocarbures, gaz carbonique et composés organiques volatils) et solides. Les particules solides sont subdivisées en 2 groupes : organique et minérales. Ce sont les particules minérales et leur concentration en métaux sont l'objectif central de cette thèse.

Le chapitre 1 *«Présentation du cadre de l'étude»* développe les différents axes principaux suivants, qui tous jouent un rôle dans la situation actuelle de la pollution atmosphérique à Santiago du Chili:

- Le contexte géographique, géologique, climatique et végétal de la ville.
- Le contexte météorologique, qui est décrit afin de comprendre la relation entre les jours de pollution maximale, et certaines configurations météorologiques spécifiques dépendant de la pression et de la température.
- L'évolution des lois et mesures environnementales de la part de l'Etat au cours des années afin de diminuer le niveau de pollution observé depuis le début des années 80.
- Dans le cadre du plan antipollution de Santiago du Chili, la liste des différentes sources polluantes, identifiées sont exposées même comme les principaux pôles industriels à Santiago et autour de la ville, caractérisés selon leur type d'activité. La pollution mesurée le long des principaux axes routiers de Santiago via des stations de mesure de la qualité de l'air, est présentée ici sous forme de carte.
- La présentation de travaux antérieurs : l'étude des deux fractions (PM10 et PM2.5) d'un point de vue minéralogique et chimique.

Le chapitre 2 « S*ites, Matériels et Méthodes* » se divise en 5 parties:

- La localisation des 4 stations de surveillance, La Paz, Las Condes, Teatinos et Macul.
- La description de l'environnement urbain et industriel des 4 stations de surveillance.
- La méthodologie d'échantillonnage.
- Les techniques analytiques utilisées: PIXE (Particle-induced X-ray emission or proton-induced X-ray emission), MEB (Microscope Electronique du Balayage) et ICP-MS (Inductively Coupled Plasma Mass Spectrometry).
- Les différentes techniques utilisées dans le traitement de la base de données.

Le chapitre 3 « *Minéralogie* » comporte deux parties:

- La première est une publication (*Morata et al.*, 2008) présentant les résultats minéralogiques et géochimiques obtenus sur des échantillons prélevés en 2004 dans les stations de Teatinos et de Macul (voir page 70-84).
- La deuxième partie porte sur les échantillonnages réalisés en 2005 et 2006 dans les stationes de La Paz et Las Condes. Cette partie compléte les résultats exposés dans la publication *Morata et al., 2008*.

Le chapitre 4 « Géochimie » est un projet de publication « Geochemical features on urban aerosols in Santiago de Chile from time-series analysis »

- Ce chapitre, après avoir présenté le contexte général de la pollution à Santiago (voir chapitre 1) présente la base de données géochimiques acquise sur des échantillons prélevés à La Paz et Las Condes. Elle porte sur 48 éléments analysés dans 202 échantillons.
- Analyse géochimique classique (concentrations, facteurs d'enrichissement) et discussions des données en termes de sources et de processus.
- Des correlations avec les données météorologiques sont présentées

- Des outils statistiques sont utilisés pour discriminer les éléments d'origine naturelle de ceux d'origine anthropogénique et pour déterminer et/ou préciser les associations élémentaires liées aux caractéristiques des différentes sources de polluants.

- Une exploration du potentiel présenté par les terres rares en terme de traçage de sources est réalisée. Des rapports élémentaires (ex La/Sm, La/Ce, La/V) semblent spécifiquement adaptés pour tracer des sources telles (pétrochimie, etc.)
- Ces résultats sont comparés avec les études précédemment effectuées à Santiago ou dans la région

Le chapitre 5 « *Discussion et Conclusion* » essaie d'intégrer toutes les informations obtenues, et de proposer des interprétations des données en terme de provenance des différentes particules.

- Une fois connues leurs origines respectives, les sources polluantes présentes dans la ville de Santiago et autour d'elle sont classées selon leur nature : naturelle ou anthropogénique et aussi en terme d'échelle de leur impact: régional ou local.
- Les facteurs météorologiques (systèmes d'haute et basse pression et température et vitesse de vents) et couplés aux émissions des sources de pollution identifiées précédemment peuvent expliquer les hautes concentrations en éléments dangereux pour la santé pas que ceux-là, tous les éléments considérés.
- Les niveaux de pollution à Santiago sont comparés à ceux observés dans certaines mégapoles d'Amérique Latine et du reste du monde. De même ils sont comparés aux normes émises par des organismes internationaux pour certains métaux particulièrement toxiques, afin d'évaluer l'efficacité des diverses politiques implémentées au cours du temps par l'état chilien et montrer les perspectives à suivre dans le programme de décontamination atmosphérique de Santiago du Chili.

Le chapitre « *Bibliographie* » comprend toutes les références bibliographiques contenues dans la thèse, excepté les références citées dans l'article publiée (Morata et al., 2008).

L'annexe A « *Impact sur la santé publique* » est un second projet de publication « Associations between Cause-Specific Mortality and Elemental Concentrations of Ambient Particles (PM2.5) in Santiago, Chile».
- La présente étude correspond à un travail d'application réalisé à partir d'une base de données robuste regroupant des données chimiques et épidémiologiques à Santiago, obtenus par le

Ministère de la Santé de Santiago. À travers ce travail, nous évaluons l'impact de certains éléments chimiques sur les taux de mortalité de la population.

- Ce travail à été développé dans le cadre de la thèse, en collaboration entre le GET, Université de Toulouse, et le Département d'Epidémiologie et Environnement de la Faculté de Médecine de l'Université d'Harvard.

INTRODUCTION

La Pollution atmosphérique urbaine

Toutes les mégapoles et métropoles du monde souffrent d'une forte pollution atmosphérique, visible quand on approche de ces villes surmontées d'un « couvercle » atmosphérique peu transparent et de couleur orangé. Cette pollution atmosphérique est aussi physiquement perceptible par des picotements plus ou moins intenses des yeux, du nez et de la gorge, traduisant l'existence de réactions allergiques. Elle s'exprime sous deux formes : des concentrations trop élevées en gaz agressifs et/ou toxiques et en particules respirables dont les effets exacts sont encore mal connus. Ce problème de pollution urbaine est devenu un enjeu majeur de santé publique, ceci d'autant plus que la majorité de la population mondiale est de plus en plus concentrée dans des mégapoles, en particulier dans les pays en voie de développement où elles ont des croissances exponentielles.

Des recherches récentes mettent en évidence de plus en plus clairement l'existence de corrélations entre l'augmentation des concentrations en polluants et l'augmentation des admissions dans les hôpitaux pour des problèmes généralement respiratoires ou cardiovasculaires (Delfino et al., 2005; Ostro et al., 1996).

Devant cet enjeu de santé publique, la majorité de ces mégapoles et de plus en plus de villes de taille moyenne se sont dotées, ces dernières décennies, d'organismes de surveillance d'un certain nombre d'indicateurs de pollution afin de pouvoir émettre des bulletins d'alerte lors de pics de pollution. Ces organismes constituent ainsi des bases de données temporelles très précieuses qui peuvent ensuite être valorisées et exploitées en relation avec des spécialistes de la chimie de l'atmosphère, afin de comprendre les causes de ces pollutions, d'identifier leurs sources et/ou mécanismes de formation et, à terme, de disposer d'arguments pour définir des politiques de réduction de ces polluants.

Les paramètres généralement suivis en continu et analysés automatiquement sont :

- Les polluants gazeux : teneurs en NO, NO_2, CO et CO_2, O_3, $SO_{2.}$

- Les aérosols solides de tailles inférieure a 1µm: ils sont collectés sur des filtres, en général sous forme d'un prélèvement tous les 24h, et leur poids de particules respirables est déterminé (µg/m^3 d'air), ainsi parfois, que leurs teneurs en C particulaire.

Bien évidemment les conditions météorologiques: T°, hygrométrie, direction du vent, etc, sont aussi mesurées.

Chaque pays a défini ses normes en termes de dangerosité et des normes ont aussi été fixées par l'OMS. Les concentrations des polluants mesurées permettent, selon des péréquations spécifiques à chaque ville/pays, de calculer un indice de pollution global, diffusé à la population. Quand l'indice global et/ou un de ces paramètres mesuré dépasse la norme locale, des états de pré-alerte, puis d'alerte sont déclanchés. Ils se traduisent d'abord par des recommandations faites aux populations les plus fragiles, puis par des mesures coercitives touchant: les vitesses de circulation et/ou le nombre de véhicules autorisés à circuler et les activités industrielles, qui peuvent être arrêtées.

Mais toutes ces actions de prévention parent au plus pressé et ne règlent pas les problèmes de fond qui nécessitent de comprendre tous les processus impliqués dans le développement des conditions de crise de pollution.

Les composants de la pollution atmosphérique

Les polluants gazeux

Les gaz polluants principaux sont:

- Les oxydes d'azote (NO et NO_2), qui proviennent des gaz d'échappement des véhicules, des centrales thermiques et électriques, des usines de fabrication d'acide nitrique, d'explosifs et d'engrais.
- Les oxydants photochimiques : l'ozone principalement mais aussi les nitrates de péroxyacétyle et les aldéhydes, qui se forment dans l'atmosphère par réaction des oxydes d'azote et des hydrocarbures avec la lumière. Ils se forment donc principalement durant les périodes de grand soleil et grande chaleur.
- Les hydrocarbures (éthane, éthylène, propane, butane, pentane, acétylène) qui proviennent des gaz d'échappement, des solvants, de l'élimination des déchets solides, et qui sont les produits dérivés de nombreux processus industriels.
- Le gaz carbonique (CO_2) issu de toutes formes de combustion.
- Les composés organiques volatils (COV).

Tous ces gaz sont reconnus comme (CO) responsables de troubles médicaux et certains sont soumis à des recommandations de doses admissibles à ne pas dépasser (Vovelle, 2000 ; Hester and Harrison, 1998). Mais ces gaz ont des durées de vie très variables dans l'atmosphère, depuis l'ozone qui est relativement instable et disparaît relativement rapidement, le CH qui peut rester 10 ans dans l'atmosphère et le CO_2 jusqu'à 120 ans. Ces durées de vie longues diminuent bien sûr l'efficacité des mesures prises pour en réduire l'impact sur la santé.

De nombreux programmes sont développés par les chimistes de l'atmosphère pour comprendre ces réactions complexes qui se développent à différents niveaux de l'atmosphère et conduisent à la formation de gaz secondaires tels que l'ozone. Les effets de la pollution sur le climat et sur les bilans radiatifs sont aussi bien étudiés. Causes et effets des polluants gazeux sont enfin bien suivis et compris à l'échelle locale, en relation avec les organismes de suivi et de recherche.

Les polluants gazeux ne seront abordés que très marginalement dans ce travail, en relation avec leur capacité à donner naissance à des particules de sels secondaires (Préndez, 1993; Eisele and McMurry P.H, 1997; Zhang et al., 2004,)

Les particules solides

Les particules solides peuvent être classées selon leur origine : lithogénique, biogénique, anthropogénique, ou selon leur mode de formation : particules primaires (déjà individualisées mécaniquement et chimiquement avant d'être prises dans la circulation atmosphérique), ou particules secondaires (qui sont, comme les polluants gazeux secondaires, formées dans l'atmosphère, par des réactions entre composés naturels et/ou anthropogéniques). Ces deux modes de classement se recoupent, les particules lithogéniques et biogéniques font partie des particules primaires, comme certaines particules d'origine anthropogénique, issues du trafic ou des industries. Les particules d'origine secondaires sont d'origine mixte ou anthropogénique et jouent un rôle important dans l'impact de la pollution sur la santé.

Les particules primaires d'origine lithogénique:

Des particules de toutes tailles sont présentes dans l'air, indépendamment de l'activité et de la concentration humaine, provenant des sols et dispersées par le vent (aérosols terrigènes ou AT). De nombreuses études portent sur les sources et les causes de remise en suspension de particules du sol, sur leur capacité de dissémination, les altitudes où ces particules peuvent être trouvées dans l'atmosphère, sur leur rôle aussi en terme de bilan radiatif (Brasseur et al., 1999).

Ainsi, on sait que le pourcentage de particules qui peuvent être arrachées à un sol dépend de nombreux facteurs, tels que la vitesse du vent, qui doit atteindre une valeur critique pour déloger ces particules, la taille de ces particules, le taux d'humidité au sol, l'état du couvert végétal et la composition minéralogique des particules présentes à la surface du sol. Il est connu aussi que les sources principales de poussières présentes dans l'atmosphère appartiennent aux régions arides et semi arides telles que le Sahara, le Moyen Orient, les déserts chinois. Mais toute région, telle que celle de Santiago, à climat méditerranéen aride et faible couvert végétal a les capacités à générer des aérosols provenant du sol, ceci d'autant plus que l'activité humaine peut amplifier les processus d'arrachement au sol et de mise en suspension (trafic routier sur pistes non asphaltées, carrières, déforestation, etc).

Les particules primaires d'origine biogénique

On trouve aussi dans l'air des particules d'origine végétale (grains de pollen principalement) ou animale (fragments d'insectes, par exemple). La présence de pollen dans l'air présente des pics au printemps et est cause de problèmes d'origine allergique (asthme, œdème.etc)

Les particules primaires d'origine marine

La présence de particules d'origine marine est connue et présente dans l'air, même à des distances assez éloignée du rivage si les vents en favorisent le transport. Ce sont principalement des petits grains de NaCl, mais des petits microorganismes ont déjà aussi été identifiés.

Les particules d'origine anthropogénique

A cela s'ajoutent les particules dues à l'activité humaine, elles aussi de tailles variables et dispersées par le vent. Elles peuvent provenir des usines, dont les fonderies et les incinérateurs, des carrières et cimenteries, des combustions de bois (brûlis en milieu rural ou chauffage des maisons) de charbon et de fioul, (chauffage individuel ou collectif), du trafic (émission des pots d'échappement – catalytiques ou non-, usure des pneus et des chaussées). Certains types de sources correspondent à des particules de signature géochimique spécifique, tel est le cas pour la combustion du bois, pour les incinérateurs et le trafic, (voir table 3) (Dictuc, 2007; Moreno et al., 2010, Engellbrecht et al., 2009; Artaxo et al., 1999). Mais certaines autres sources ont chacune leur signature propre, tel est le cas des usines, des hauts-fourneaux et d'autres des signatures « larges » complexes, avec la présence d'éléments chimiques communs à plusieurs sources polluantes. Ceci complique l'identification des différentes sources au sein d'une pollution urbaine globale qui intègre toutes ces composantes.

Taille des particules et temps de résidence

L'intensité, la dangerosité d'une pollution sont aussi contrôlées par sa durée, elle même tributaire du temps de résidence des particules qui portent cette pollution.

Les temps de séjour des particules dans l'atmosphère varient suivant leur taille. Ainsi les petites particules (0.001-0.08µm) ont un temps de résidence inférieur à une heure car elles coagulent et précipitent rapidement. Les particules dont la taille est comprise entre 0.08 µm et 1µm ont des temps de résidence compris entre 4 et 40 jours quand celui des particules de taille à 1 µm est de quelques heures. On peut voir qu'une pollution portée par des particules entre 0,08 et 1 µm sera plus nocive dans la mesure où elle restera disponible plus longtemps.

La longueur du voyage qu'effectueront ces particules est inversement proportionnelle à leur taille (Warneck, 2000). Les grosses particules (> 5 µm) sédimentent rapidement et ne se déplacent pas au delà de 500 km, même si, lors d'événements particuliers comme les fronts atmosphériques tropicaux, de telles particules peuvent faire plus de 5000 km. C'est le cas des poussières (aluminosilicates) sahariennes que l'on retrouve en Europe et dont la taille moyenne est de 10 µm (Wallace and Hobbs, 1977). Les particules plus fines peuvent être transportées sur de plus longues distances, c'est pourquoi on retrouve des traces de contamination anthropique par les métaux dans les glaces de l'arctique et de l'antarctique (Wolff et Suttie, 1994 ; et article de synthèse de Boutron et al., 1994).

Après leur transport, les particules finissent par se déposer, soit par dépôt sec continu (sédimentation ou impaction sur des obstacles) soit par dépôts humides lors des épisodes pluvieux ou neigeux. celles qui peuvent se sédimenter rapidement sur le sol sont les « free fall particles » (FFP). Leur effet polluant ne doit pas être négligé. En effet, des particules assez grosses sortant de cheminées d'usine et retombant sur les sols environnants sont sources de pollution potentielle de ces sols, des cultures qui s'y développent, des eaux libres. Mais elles ne seront pas abordées dans ce travail.

Les particules solides respirables

Les particules qui nous préoccupent ici sont celles qui sont respirées par les humains, parce que leur durée de résidence en suspension dans l'air est relativement important en raison de leur taille. Les particules solides respirables sont classées par commodité en 2 groupes : les particules de taille aérodynamique inférieure à 10 µm (PM10) et les particules de taille aérodynamique inférieure à 2,5µm (PM2,5).

On pressent que le rôle des nano particules peut être important, quelle que soit leur nature chimique, car elles sont très petites donc pénètrent loin dans l'arbre respiratoire. Elles peuvent contribuer à disséminer des métaux adsorbés sur leur surface. Il vient d'être montré qu'elles jouent un rôle catalytique dans la synthèse de gaz précurseurs de l'ozone et contribuent à la dissémination de ce gaz (Journal du CNRS, 2010). Elles jouent enfin, mais c’est hors de notre propos, un rôle dans les bilans radiatifs de l’atmosphère. Il faudra dans un avenir proche s’en préoccuper mais il n’existe pas actuellement de système pour les prélever simplement en routine. Il faut mentionner spécifiquement les nano particules carbonées, provenant principalement des pots d’échappement de tous les véhicules, mais aussi des combustions dans l’industrie ou les foyers domestiques et de l’usure des pneus. Ce sont ces particules qui recouvrent complètement tous les filtres en milieu urbain.

Toutes ces particules dites respirables (PM10, PM2,5, nano particules) entrent l’arbre pulmonaire et peuvent, selon leur taille, être bloquées par le mucus à différents niveaux de cet arbre : nez, gorge, trachée, bronches, et sinon atteindre, pour les plus fines, le fond des alvéoles. A chaque niveau elles causent, lorsque leurs concentrations sont importantes, des problèmes de santé publique.

Bien évidemment, toutes les origines listées précédemment dans le paragraphe général sur les aérosols solides se retrouvent présentes dans la classe spécifique des particules respirables. Les proportions des différentes origines (lithogénique, biogénique, etc) peuvent être contrôlées par la taille des particules, mais assez peu de travail existe là dessus (Morata et al, 2008).

Les particules respirables et leur impact sur la santé

Les particules qui se retrouvent dans le corps humain, que ce soit dans l’arbre respiratoire ou dans le système digestif (par ingestion des mucus provenant de l’arbre respiratoire), agressent l’organisme de deux manières différentes :

- Mécanisme physique : les particules irritent les différents niveaux de l’arbre respiratoire et, pour les plus petites, finissent au niveau des alvéoles avec deux effets possibles : colmatage (et développement d’insuffisance respiratoire) ou lésion au niveau des cellules (cancers liés à l’amiante par exemple).
- Mécanisme chimique : les particules sont, de par leur composition chimique propre ou par leurs propriétés adsorbantes, porteuses d’éléments chimiques qu’elles véhiculent à l’intérieur du corps. Quand il s’agit d’éléments toxiques, tels que As ou Pb, la respiration et l’ingestion de ces particules peut contribuer au développement de pathologies.

Mais pour l’instant, les épidémiologistes en sont seulement à noter les corrélations entre les nombres d’admission à l’hôpital pour problème cardio-vasculaire ou respiratoire et les concentrations en particules respirables dans l’air. Assez peu d’études vont au delà en mettant en évidence des corrélations entre l'augmentation de la concentration d'un élément chimique et l'augmentation de certains risques sanitaires (Cakmak et al., 2009; Ostro et al., 1996). Ceci montre à l'évidence le besoin crucial d'une meilleure connaissance de la nature, physique et chimique, de ces particules respirables. Cette meilleure connaissance sera utilisée de deux manières :

- Les médecins utiliseront directement les caractérisations physiques mais surtout chimiques pour mieux comprendre le rôle des particules dans les maladies observées.
- L'identification fine des sources, quand elle est possible, permettra aux organismes en charge de développer les actions ciblées de prévention et de lutte contre la pollution.

Il y a donc un besoin criant de données minéralogiques et géochimiques statistiquement significatives sur chaque ville/région polluée. Tel est l'enjeu majeur abordé dans ce travail, appliqué au problème aigu de la pollution atmosphérique de Santiago du Chili.

Objectifs de la thèse

Le travail présenté ici repose sur l'acquisition et l'interprétation de données géochimiques exhaustives obtenues sur des échantillons prélevés dans deux sites sélectionnés de cette mégapole pour leur représentativité, l'un étant en milieu populaire urbain dense, mélangeant habitat et industrie, l'autre étant en milieu résidentiel des classes aisées, faiblement urbanisé et bien végétalisé, sans industrie, et seulement perturbé par de grands axes routiers. De plus le premier site est au centre ouest de la conurbation quand le deuxième est au pied de la cordilière andine, à l'extrémité orientale de l'agglomération. Ces positions relatives auront toute leur importance quand il sera tenu compte des directions les plus fréquentes des vents.

Dans chacun de ces deux sites un échantillonnage sur deux ans a été fait, afin d'être représentatif à la fois des jours et saisons les plus et les moins pollués. Les concentrations en une quarantaine d'éléments chimiques ont été déterminées sur ces échantillons. Des données complémentaires ont été acquises par microscopie à Balayage (MEB) en couplage avec de la spectrométrie (EDS), afin de proposer des interprétations minéralogiques des particules observées.

Grâce à cet ensemble de données, l'objectif précis de ce travail est d'une parte la caractérisation minéralogique et géochimique du matériel particulaire (PM2.5 et PM10) et l'identification de sources émettrices de ces polluants afin de diminuer leurs émissions et, ainsi, diminuer leur impact sur la population.

Les objectifs sont abordés en trois axes principaux :

1. La caractérisation minéralogique et géochimique PM10 et PM2.5. qui comprend:

- Le Monitoring (suivi en continu) géochimique des PM10 et PM2.5 pour comparer les deux sites de prélèvement, les deux granulométries.
- La caractérisation minéralogique et morphologique des fractions PM10 et PM2.5.
- La quantification les niveaux de concentration d'un certain nombre d'éléments, durant les épisodes de pollution et en situation normale dans les deux sites, ceci dans les deux granulométries, PM10 et PM2,5.

2. L'identification de sources qui est basée sur des signatures géochimiques avec:

- La discrimination de sources anthropogéniques et naturelles en utilisant le concept de « facteur d'enrichissement » pour quantifier les enrichissements anormaux en certains éléments chimiques par rapport à la contribution lithogénique moyenne provenant de l'usure et l'altération de la croûte continentale.
- L'identification des sources dans un signal complexe grâce à des traitements statistiques, seuls capables d'interpréter de grosses bases de données multiparamètres par identifier des associations remarquables d'éléments chimiques à interpréter en termes de sources.
- Les signatures géochimiques des sources par le couplage des informations géochimiques extraites dans les points précédents, avec les interprétations minéralogiques et l'utilisation des signatures en Terre Rares (nouveaux traceurs) pour la connaissance des sites de pollution potentiels, et celle des vents pour proposer des interprétations à tel ou tel épisode de pollution.

3. Evolution temporelle des concentrations chimiques a court et a long terme:

A court terme (2004-2005) on détermine :
- des variations saisonnières et annuelles
- le rôle des conditions météorologique

A long terme (1996-2004/2005) on évalue:

- l'impact des politiques publiques en matière de lutte contre la pollution en comparant les données acquises avec celles déjà publiées sur Santiago.

CHAPITRE 1: PRESENTATION DU CADRE DE L’ETUDE

1.1 Introduction

L'introduction du manuscrit, a présenté les généralités sur les particules respirables présentes dans le matériel particulaire (MP) en suspension dans l'air : leurs origines diverses (lithogéniques, biogéniques ou anthropogéniques (organiques ou inorganiques)), leurs temps de résidence, etc. Il est important maintenant de connaître, spécifiquement pour la région de Santiago, tous les paramètres particuliers qui peuvent influer sur l'origine, la quantité, la répartition spatiale de ces particules respirables.

Ainsi, pour comprendre et interpréter correctement tout essai de caractérisation des particules d'origine lithogéniques, il est important de contraindre l'environnement géologique, pédologique et végétal qui va conditionner la nature, l'origine et les conditions de dissémination de ces particules.

La génération de particules anthropogéniques leur nature et leur distribution dépendent, entre autres facteurs, du type et de la répartition des activités industrielles, des routes et des sources polluantes spécifiques comme les mines, les hauts fourneaux, les raffineries, les incinérateurs, les centrales thermiques.

Enfin, la distribution spatiale et la concentration des aérosols dépendent de temps de résidence des particules dans l'air, qui lui-même dépend des conditions météorologiques spécifiques, et de l'intensité et des directions des vents. Une présentation synthétique du contexte météorologique et des régimes d'évents est ainsi proposée.

D'autre part, notre étude, limitée aux années 2004 et 2005, ne peut pas être interprétée et commentée sans tenir compte des actions menées par les agences gouvernementales depuis les années 1980 pour réduire la pollution. De plus, le développement de réseaux MACAM dans les années 1990 a permis, de constituer une base de données de mesures d'un certain nombre de paramètres (concentrations en différents gaz, en PM totales, etc.) qui seront précieuses dans notre étude et intégrées à nos interprétations.

L'objectif du présent chapitre est donc de fournir au lecteur toutes ces informations.

1.2 General Context

The large economic growth of the city of Santiago in the last decades has been accompanied by the expansion of all residential, commercial and industrial areas (Romero et al., 1999). The subsequent dispersion and increase of pollutant sources have damaged the quality of the environment. Santiago thus presents a very high level of pollution.

One of the major environmental problems is the resulting poor air quality within the city and its suburbs. This situation causes many health problems and several authors have pointed out the relationship between air pollution and mortality respiratory and cardiovascular problems being the principal causes (Ostro et al., 1996; Ilabaca et al., 1999; Cifuentes et al., 2000; Pino et al., 2004; Roman et al., 2004; Prieto et al., 2007; Cakmak et al., 2007, O'Neill et al., 2008). Besides the role played by different gases that will be listed but not be considered in this specific study, particulate matter (PM) appears to play a critical role in these pollution-related health problems.

If the size and concentrations of particulate matter (PM) have been associated with adverse health outcomes, the specific components that are harmful are not well characterized and their role, in Santiago as well as in major polluted cities, is not yet clearly understood (Bell et al., 2005). It is only recently that appeared articles demonstrating the incidence between an increase of metal concentrations (i.e. Ni, Zn) and an increase in cardiovascular and respiratory mortality (Cakmak et al., 2009; Valdes et al., in preparation, appendix A).

It is in this context that our study on the mineralogical and geochemical characterization of breathable particulate matter has been conducted, in order to quantify metals concentrations in the PM10 and PM2.5 fractions, and to attempt a characterization of the potential sources of these metals.

1.3 Topography

Santiago de Chile, the capital of Chile, is located at 33.5° latitude S and 70.8° longitude W (fig 1). More than 7 millions inhabitants, corresponding to 43 % of the population of Chile are living in this metropolis, located in a confined basin between the Andes Mountains to the east and the Coastal range to the west (fig 2).

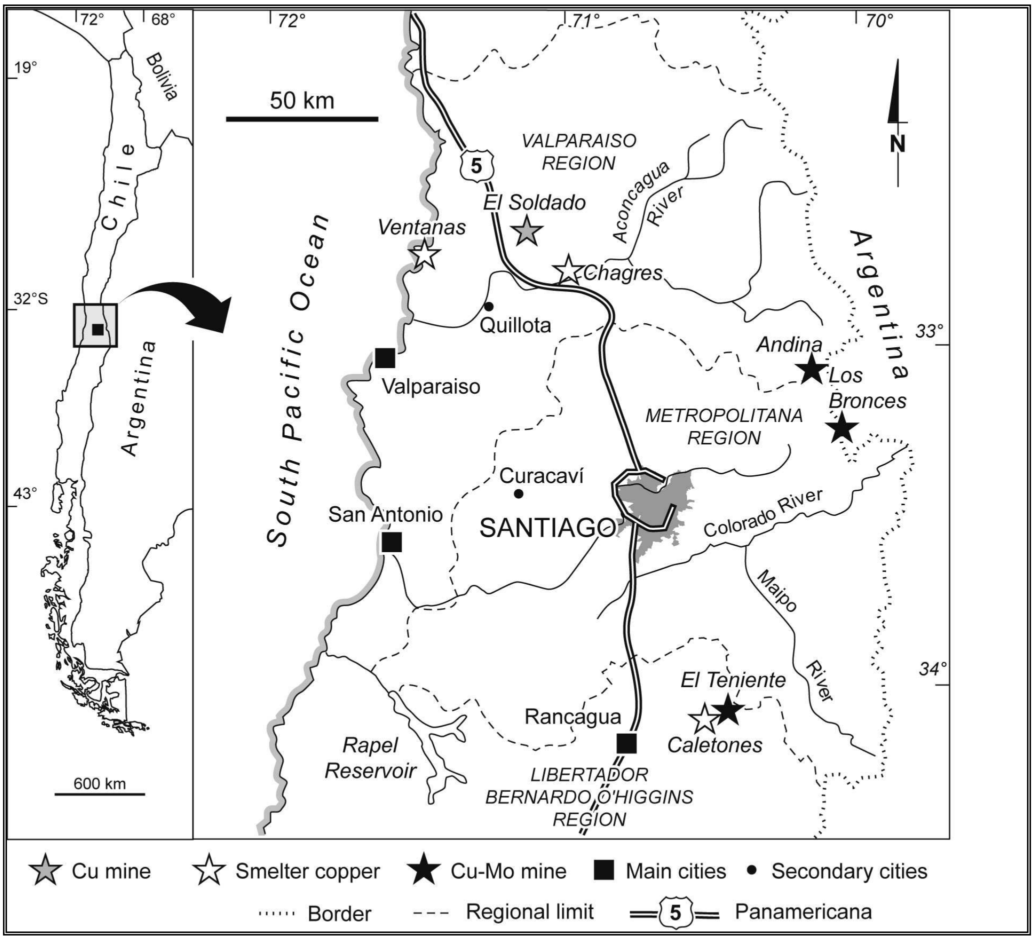


Figure 1: General location of Santiago (modified from Sernageomin geological map 1:100000; 1999) with mention of the main roads, cities, mines and smelters.

In fact, the geographical context at Santiago is characterized by geomorphologic units that are, from west to east: the Coastal Mountains, Central Depression and Andes Mountains, the later divided in "Andes Precordillera" and "Andes Cordillera".

The "Andes Precordillera" starts at the outskirts of Santiago city and riches 3000 m.a.s.l. with the Cerro San Ramon (approx. 3200 m). The Andean orogen is recent and hosts both active, inactive and extinct volcanoes, the altitude of which is increasing eastward, with the San Jose (5.856 m), Tupungatito (5.913 m), and Tupungato (6.570 m) volcanoes, not to mention the non volcanic Aconcagua, highest peak of South America, (6.962m) which is only 100 km N-E of Santiago. The Maipo and Mapocho valleys cut the Andes Mountains, south and north of Santiago respectively. The Maipo valley begins at the foot of Maipo volcano and the Mapocho river is built by the confluence of the *San Francisco* and *Molina* rivers, around 33°S and 70°W. Both run west ward and cross Santiago city. The regime of these rivers is fluvial-snow.

The Coastal Mountains reach 2000 meters and are cut by the Maipo Valley which allows oceanic contributions to reach the city. They act as a "climatic wall" that influences the weather at Santiago by limiting the effect of the west winds.

Santiago is localized in the Central Depression between the Coastal Mountains and the Andes Mountains. Besides these two important topographical heights, Santiago basin is also bordered by lower reliefs that are: the Chacabuco Mountains to the north and the Angostura and Chada Hills to the south (both < 1.500m) (fig 2).

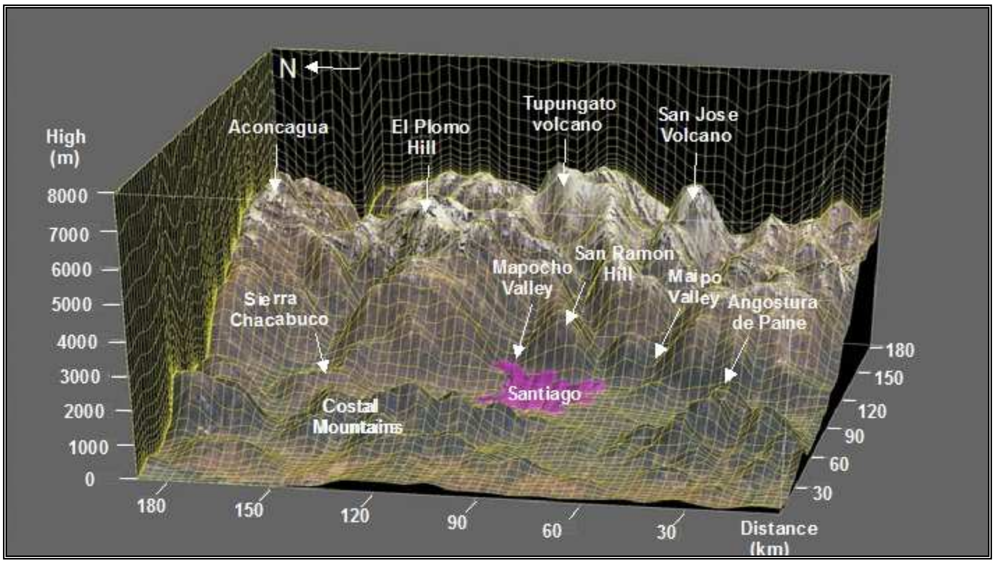


Figure 2: Principal topographical features of the Santiago basin (modified from Dept. Geophysic., Univ. Chile)

Santiago basin extends on 70-80 km N-S and 30-40 km E-W (Sandoval et al., 1993) (fig 2 and 3). Altitude of Santiago city varies from 400m a.s.l. to the west and the coastal range, to 800 m towards the Andes foothills. Santiago basin is punctuated by island hills, such as Lonquén (1028 m), Chena (950 m) and Renca (903 m) (fig 3). A mountain chain penetrates the city itself, with the Manquehue (1650m) and San Cristobal (880m) hills. The basin is crossed by rivers and streams generally running down the Andes towards the Pacific Ocean. The most important are the Mapocho river to the north and the Maipo to the southeast. All these morphological features will play a key role in the atmospheric circulation over Santiago area.

1.4 Geology

Santiago basin is emplaced on Middle to Upper Pleistocene alluvial deposits (fig 3). To the east, these deposits intergrowth with colluvial and alluvial deposits (Qc and Qap), while to the west they grade to lakes deposits (Ql). These deposits are composed of gravels and sands with a minor contribution of fine sediments (sands, mud and clays) which increases westwards. Andesitic to basaltic lavas (28-20 Ma) with interlayers of calcareous rocks outcrop in the northeastern part of Santiago basin (OlMa; fig 3). These formations occur also as intrusions (20-19 Ma) such as the above-mentioned Manquehue hill. The Pudahuel ignimbrites (Qip, Middle Pleistocene) outcrop to the west of Santiago basin, ending at the eastern border of Coastal Mountains and spreading southwards towards Maipu city (fig 3). This formation overlays the cretaceous (Kivn) Veta Negra Formation (porphyritic and aphanitic andesites lavas with calcareous interlayers) and other volcano-sedimentary sequences (Kivn, Kilp), that are intruded by granitoides dated between 80-100 Ma (Kd and Kmd).

As mentioned in figure 3, the Cretaceous volcanic and volcano sedimentary formations from the Coastal Mountains eastern border host ores that are or have been exploited. These N-S metallic ores are principally gold, iron and copper deposits and in a second order ore of Pb and Zn. On the contrary, the presence of metallic ore is poor in the Andes Mountains. Indeed, there are only some known veins of copper-gold deposits which were sites of small scale mining in the past. As an exception, 150 km to the north east of Santiago, an important center of mining activity exists and will be presented in detail later (see 1.8.2). Many quarries (limestones, volcanic rocks for construction, gypsum, clays) exist in the sedimentary formations at the foothills of the two mountain ranges and in the central basin.

Additionally, figure 3 shows the location of artificial deposits, organic and inorganic (urban, industrial, mining activities deposits, etc). They are potential pollutant sources and will be listed in more details later.

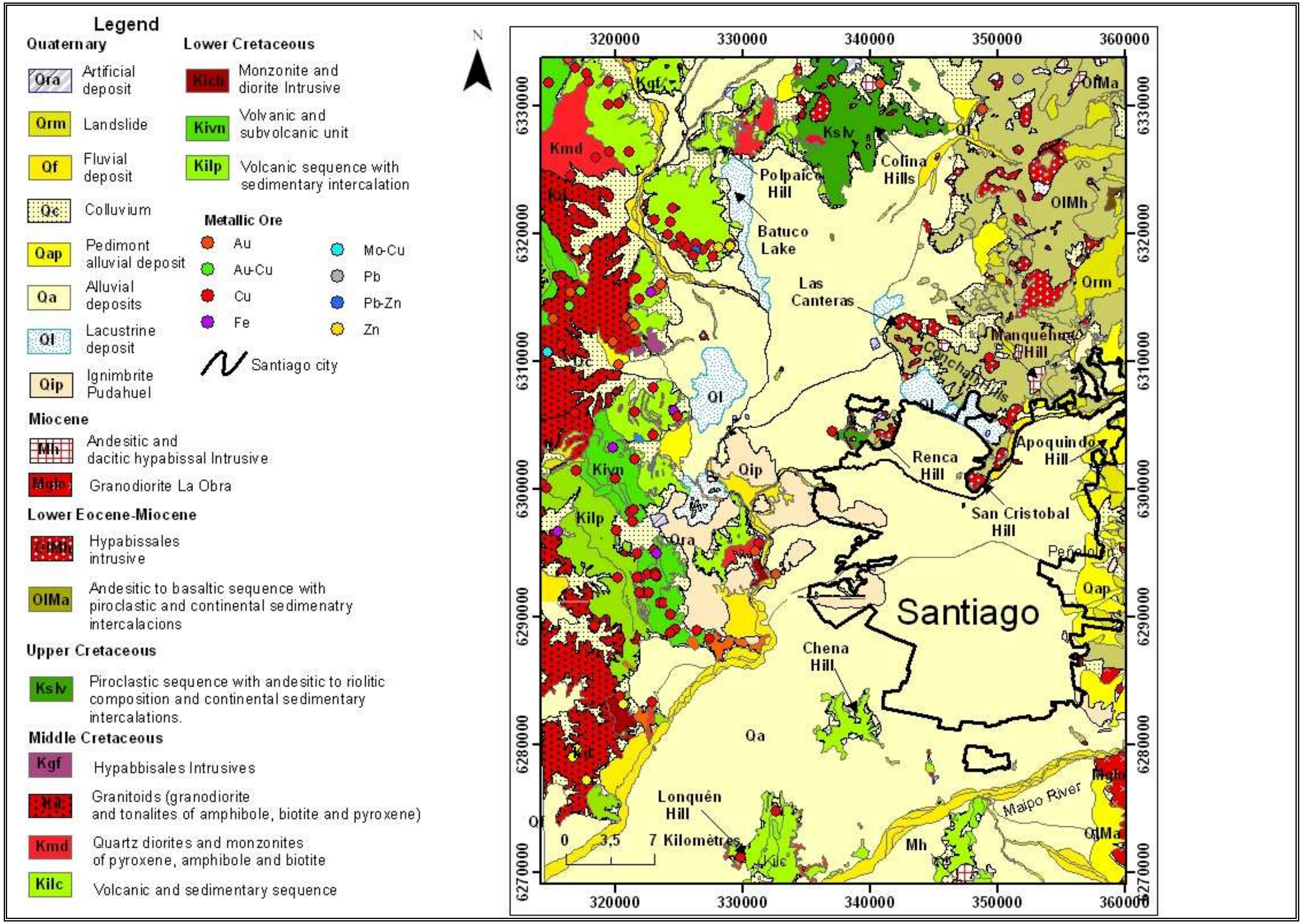


Figure 3: Schematic geological map of the Santiago area (35°) (from geological map of Sernageomin, 1999, 1:100000)

1.5 Climate and vegetation

Climate in this central part of Chile is typical mediterranean semi arid, with annual average rainfall around 400 mm, and average temperatures between 10°C (winter) to 20°C (summer). The associated original vegetation in the central basin is mostly composed of spiny bushes and small trees (Acacia Caven (espinos), Prosopis chilensis, Proustia ilicifolia (huañil), Maytenus boaria (maitén), Salix babylonica L (sauce), Escallonia alpina (ñipa)). Grass cover and annual flowers exist only at springtime, while the rest of the year, natural areas do not have any continuous vegetation cover. This observation is important for solid aerosol genesis, as it will be seen later.

On the mountain-side of Andes Mountains, vegetation of middle and low altitude (500-1000 m) is composed of Lithraea caustica (litre), Quillaja saponaria (quillay), Colliguaja odorifera (colliguay), Peumus boldus (peumo), Chusquea quila (quila), Triglochin_spp (coironcillo), Aristotelia chilensis (maqui), etc. Flowers such as Pasithea coerulea (azulillo), Alstroemeria angustifolia (lirio del campo) and Mutisia (clavel del campo) are also present and constitute the typical vegetations observed in this eastern part of Santiago. On the coastal mountains side, there are isolated forests characterized by: Azara petiolaris (maquicillo), Schinus montanus (litrecillo), Nothofagus macrocarpa (roble de Santiago), Guindilia trinervis (guindillo), Acacia caven (Espinillo) and also Chusquea Quila (quila), Peumus boldus (Peumo), Quillaja saponaria (quillay), and they contribute to create a localized micro climate around of Santiago.

Between 1989 and 1998, Santiago surface increased from 38.958 to 52.333 ha (Romero et al, 1999). This expansion was developed in all directions, climbing up ravines and rivers at the Andean foothills. To the south and southwest flatter zones, the expansion was on the farm and natural areas. As said before, soils around Santiago have a high agricultural capacity, good permeability and sufficient organic material. In 1998, 34400 ha were constructed, among which more than 56% were taken off agricultural soils and 42% off the dense vegetation areas. On the contrary, the use of areas with scarce vegetation, typical from Mediterranean and semi arid of central Chile, corresponds only to 20% of the total.

1.6 Meteorology

The general atmospheric circulation that affects Central Chile is controlled by a major N-S (tropical-polar) exchange, on which a E-W (mountain-ocean) exchange is superimposed. These main circulation factors, together with regional and local factors such as local topography will control the spatial and temporal features of pollution over Santiago. The main concepts displayed in this section are taken from Ulriksen (1993), Rutllant and Garreaud (1995), Merino (personal communication, 2010) and Sandoval (1993).

1.6.1 Large scale atmospheric circulation

In the general N-S atmospheric circulation (Ulkrisen, 1993), all year round the upward branch (warm and moist) of a convection cell sits over the Equator while its downward branch (cooler and dry) produces a high pressure system near 30º latitude (fig 4). As a consequence, an anticyclone, known as the Semi Permanent Pacific Anticyclone, with hot and dry air, is continuously acting in front of the South American subtropical coasts and over the land, centered at 30° latitude. Nevertheless, it does not reach the earth surface, which is covered by a cold and damp air mass, of variable thickness (100 -1500 m) related to ocean (and continent) evaporation processes. It induces a thermal inversion layer which blocks mixing between the two air masses.

Meanwhile, cold air masses are sitting over the ocean and southernmost America at high latitudes. In winter times, these cold air masses go further north, towards Central Chile and the Semi Permanent Pacific Anticyclone region. The two air masses interfere in a transition zone called “polar front” which fluctuates between 40°-60° lat S but will reach 30°lat S in winter. It is a zone of horizontal whirlwind or depressions with abundant cloudiness, precipitations, strong winds, and storms.

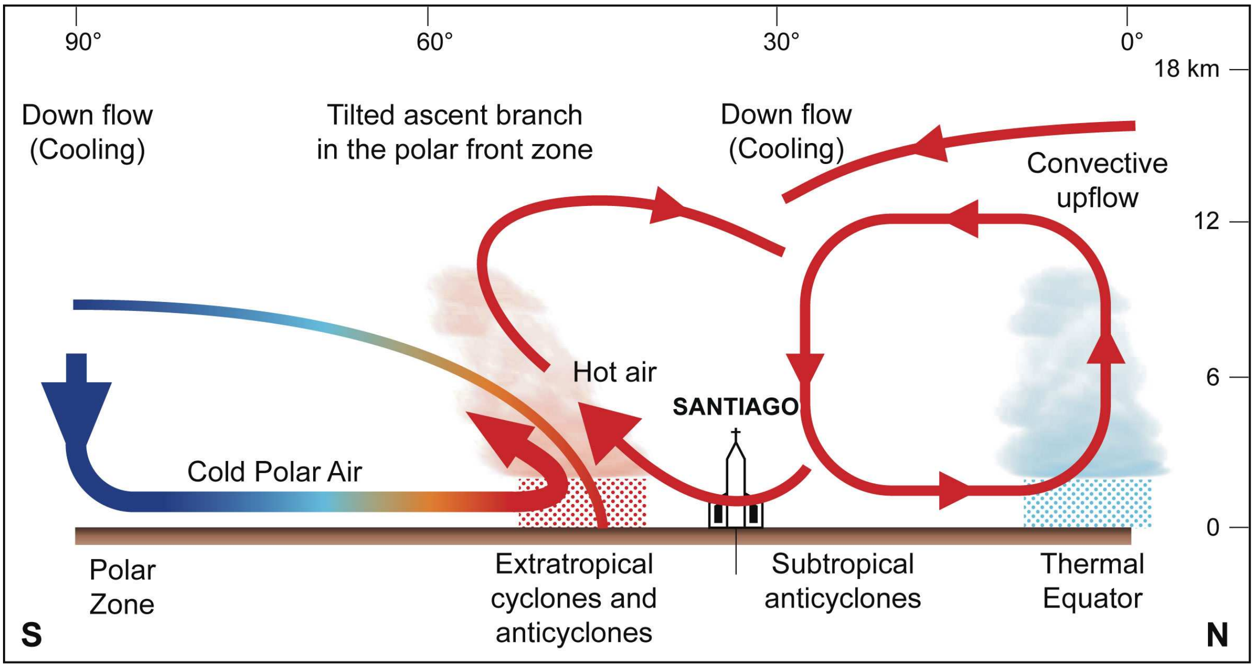


Figure 4: General N-S circulation, showing the position of Santiago with respect to the main atmospheric zones. (modified from Sandoval et al., 1993).

1.6.2 Local flow

As, most of the year, the Semi-Permanent Pacific Anticyclone remains over Central Chile and the thermal inversion layer is present, this region displays a moderate wind regime. Air circulation in Santiago basin is thus controlled mainly by local, low-velocity winds, among which the ground solar heating which creates vertical air motions within the mixing layer over the basin.

1.6.2.1 Seasonal variations

Applying the GEOrient 9.4.0 program to the DGAC data base (www.meteochile.cl), we have plotted the wind directions measured for 2004 and 2005 (fig 5). Wind direction varies from NW to NE and from NW to SE during cold months (April to September) while south winds are dominant during warm months (October to Mars). This feature could play a role in the pollutants dispersion over the basin within the mixing layer, during the cold month, as these north winds will carry southward all pollutants emitted by the industrial district north of Santiago (fig 11).

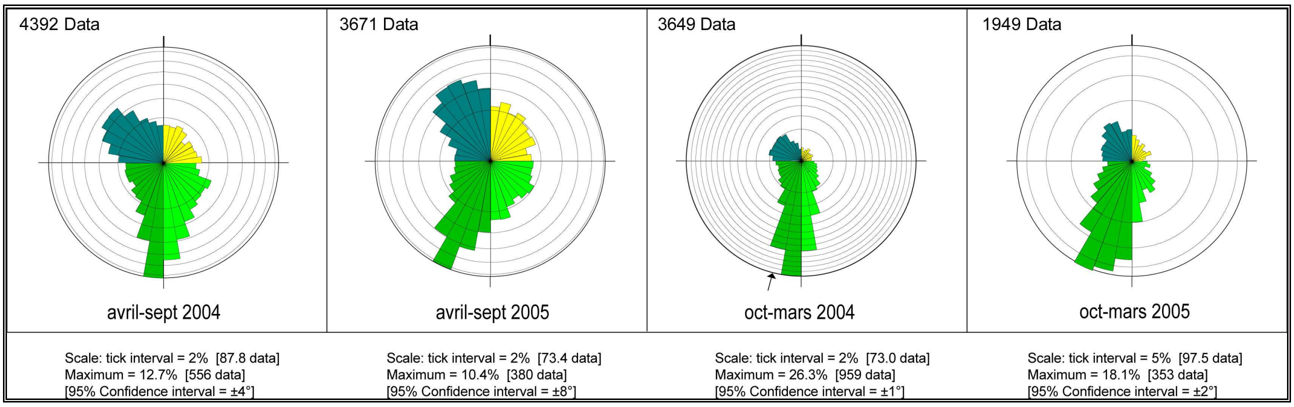


Figure 5: Frequency wind roses between cold (April to September) and warm (October to Mars) seasons in 2004 and 2005. Diagrams for the cold seasons rest on 4392 data in 2004 and 3671 in 2005. For the warm seasons they rest on 3649 data in 2004 and 1494 in 2005. Each interval (tick) corresponds to 2%. The maximum values are indicated in each diagram. This data set was taken from DGAC data (www.meteochile.cl) and MACAM network.

1.6.2.2 Daily variations

The effect of local thermal breezes whose intensity and direction vary during the day is illustrated in figure 6a, while figure 6b shows that this variation of wind velocity is strongly correlated with the thickness of the mixing layer (b) with a maximum between 11 a.m. and 4 p.m. daily.

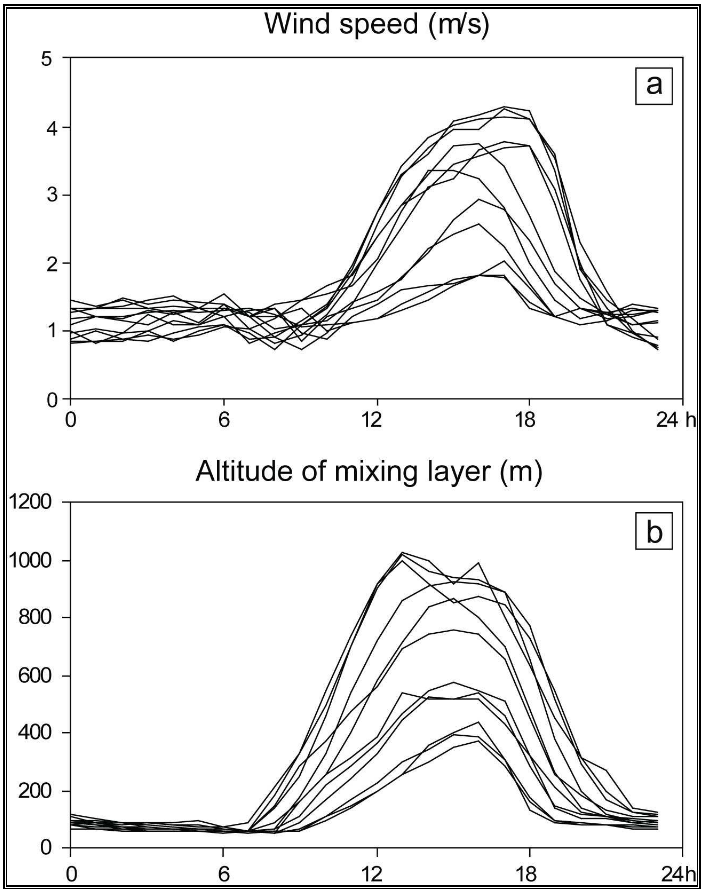


Figure 6: a) variation of thickness of the mixing layer over Santiago; b) Hourly variation of atmospheric boundary layer. (from CENMA, 2009).

In order to check the effect of these hourly variations upon pollutant masses dispersion during winter time, we analyzed the main wind directions during three time periods of the day: 00-05 a.m., 6-11 a.m. and 2-6 p.m. for 3 months (May, June and July) that are representative of winter conditions. From 00:00h – 5:00h, when wind velocity is around 0.5 m/s (fig 6a), the principal directions in decreasing order are from NW, SE, SW and NE (fig 7a) with a frequency percentage of: ~50%, 20%, 16% and 14%, respectively. During the morning (6:00h – 11:00h) when the wind velocity is around 1m/s (fig 6a) NE winds are reinforced (~23%). During the afternoon (14:00h - 18:00h) the principal wind direction is SW (~65%) with a minor contribution of wind from the North (NW and WE) (fig 7a). These statistical observations are consistent with daily observations as shown in figure 7b. These air movements from downtown to mountain during the day and the opposite way during the night have already been mentioned (Gramsch et al., 2008; Ulriksen, 1993).

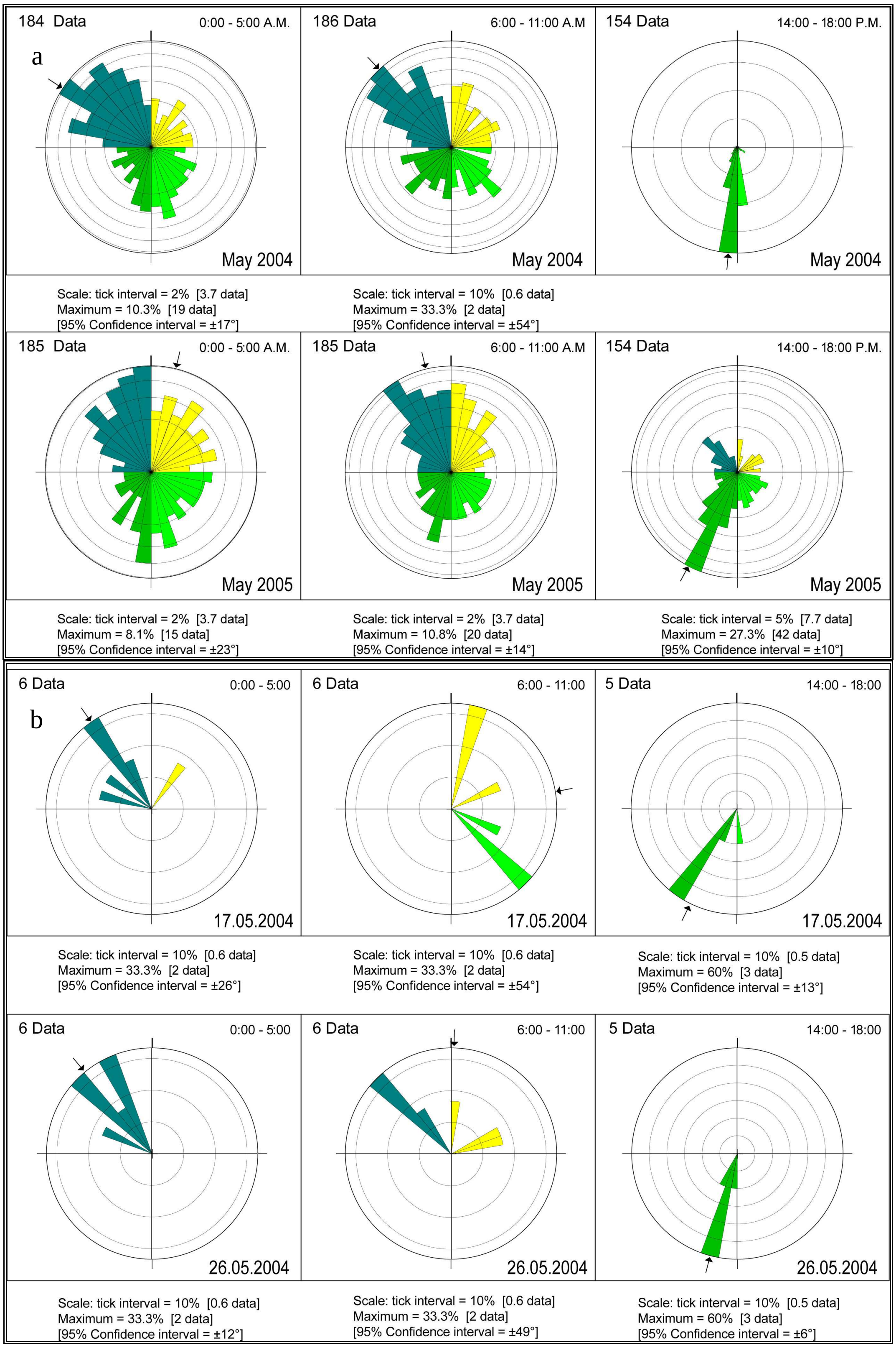


Figure 7: Data on wind directions in winter during 3 time intervals: 0 to 5 am, 6 to 11am and 2 to 6pm. a) Statistical data on May 2004 and May 2005, b) data for 2 days of May 2004.

As a consequence of these wind changes during the day, both in intensity and direction, pollutants influence is not limited to their close surrounding as they undergo significant transfer at the basin scale while being blocked within the mixing layer.

1.6.3 Definition of episodes of contamination.

The level of contamination is determined from the amount of breathable particles (PM 10) present in the air. The scale ranging from 0 to 500 µg/m^3 has 6 levels from fair to emergency (table 1) to which regulations to traffic and industries are defined by local authorities.

ICAP denomination	ICAP scale	PM10 µg/m^3 (24 h)	level	Episode
0-100 Good	0	0	0	/
101-200 Regular	100	150	0	/
201-300 Bad	200	195	1	Alert
301-400 Critical	300	240	2	Pre-emergency
401-500 Dangerous	400	285	2	Pre-emergency
> 501 Exceed	500	330	3	Emergency

Table 1: Definition by the International Carbon Action Partnership program (ICAP) of the 6 levels of pollution in function of the PM10 concentrations (taken from Health Ministry (MINSAL),1988. (www.asrm.cl).

As an example, figure 8 displays frequency histograms for the number of days with alert, pre emergency and emergency, between April 1 and September 17 of the years 1997 to 2009. Actually it is worth noting the clear decreasing trend, even if not constant. Our samples were collected in 2004 and 2005, where average concentration in PM 10 was 80µg/m^3 and 77 µg/m^3 respectively. In addition, 2005 was one of the years with the smallest number of pollution episodes.

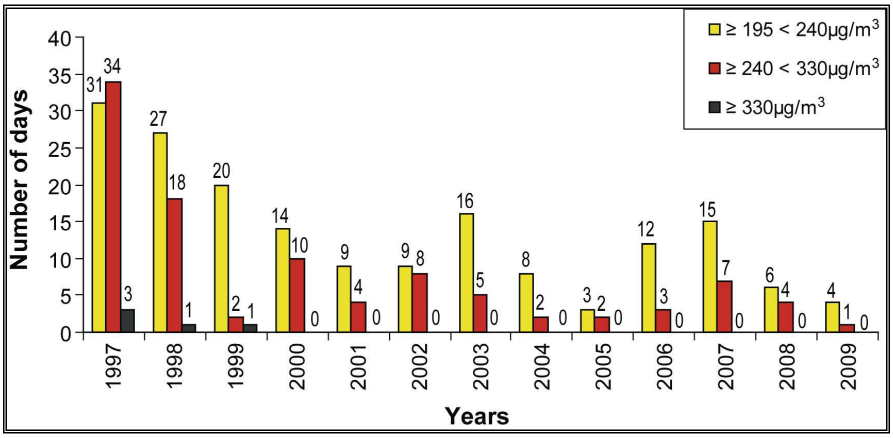


Figure 8: Numbers of days per year with episodes of contamination between 1997 to 2009 (from CENMA, 2009).

1.6.4. Meteorological conditions associated with episodes of contamination

Around 20-50 frontal systems (as described previously) reach central Chile in winter time (2004: 26; 2005: 45 from CENMA, 2009). Each frontal system first induces a better ventilation in Santiago basin and subsequently lowers contamination levels. But, a coastal (west) barometric low-pressure system is thus induced, characterized by forced air subsidence (downflow) in the occidental slopes of the Andes Mountains. This subsidence reestablishes the thermal inversion layer then reduces again the basin ventilation, which explains the association between coastal lows and critical episodes of contamination (Rutllant and Garreaud, 1995). These recurrent episodes of high contamination are associated with weak winds, strong stability of the thermal inversion layer and thin mixing layer.

Within this general scheme, different types of pollution episodes are identified by the meteorologists, which correspond to variations in this E-W barometric system. They are referred to as types H (high pressure), BPF (Before Frontal System) or mixed H-BPF (table 2). H and BPF episodes represent 70% and 30% of the total winter contamination episodes, respectively. Mixed H-BPF episodes usually start as H and finish as BPF.

Parameters	**BPF**	**H**	**H-BPF**
P°	low	high	mixing
T°	low	high	mixing
HR	midle	low	mixing
Wind	midle	midle	mixing
Clouds	high	low	mixing
Ventilation	bad	bad	bad

Table 2: Abstract of specifique metreological conditions at Santiago de chile. BPF: Before pre-frontal system and H: High pressure H-BPF: combined system.

Episode H conditions

Around the latitude of Santiago (fig 9) a large area of high pressure and temperature is installed over the land, with its base being around 500m over the ground. At the same time, at lower levels, the coastal low propagates from north to south, with a reduced vertical thickness. At the front of this coastal low, Santiago presents clear skies, east winds, high temperatures, and low humidity. The inversion layer is very stable, the mixing layer just below it is quite thin and ventilation quite low.

At the final phase of the coastal low, the east component weakens until its disappearance. After that, west circulation is associated with an ascent of the base of the subsidence thermal inversion. It increases the thickness of the surface mixing layer allowing the marine air advection to reach Santiago basin.

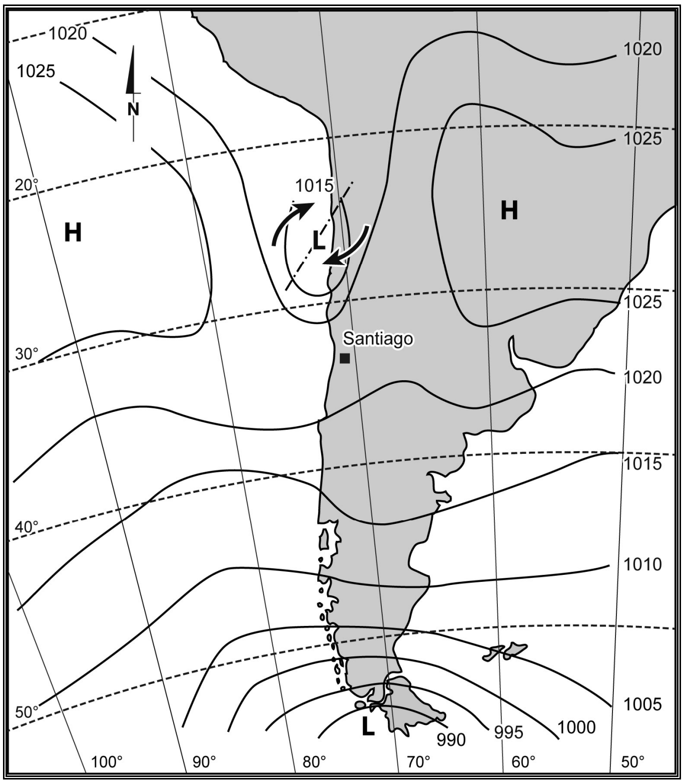


Figure 9: Location of High and Low Pressure centers over South America and especially Central Chile (from Sandoval et al., 1993). H: High pressure Center; L: Low Pressure Center. The arrows show the wind directions.

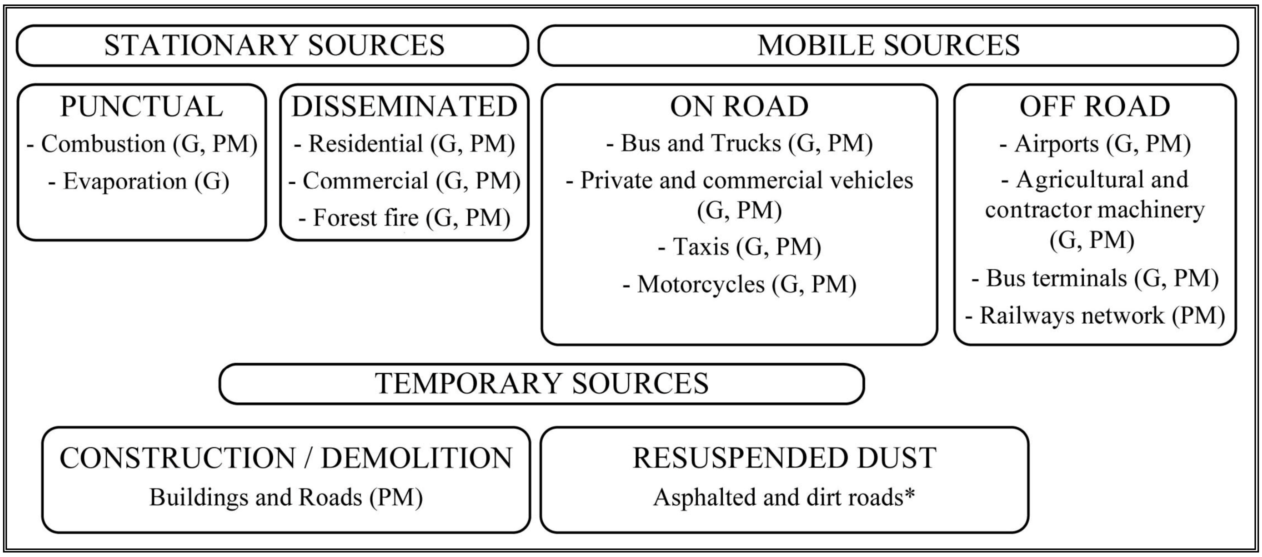
Episode BPF conditions

This type of episode is defined by its specific prefrontal conditions. In the BPF configuration, a Low Pressure Center is set to the east of the Andes Mountains while a High Pressure (cold) Center moves between Eastern South America (Argentina) and the Atlantic Ocean. This condition is usually associated with clouds and low ventilation. The mixing surface layer is reduced, and the wind is almost non existent. Clouds inhibit the thermal breeze between valley and mountain, and in addition, prefrontal descent winds from the northeast have a tendency to stop the south-southwest winds during the daily cycle.

1.7 Inventory of the primary sources involved in air pollution in Santiago: sources categories

This paragraph presents an exhaustive compilation of all primary pollution sources. Following the consulting group who did it: DICTUC (Direction of Scientific and Technological Investigations of the "Pontificia Universidad Catolica de Chile"), they are presented as stationary, mobile and temporary sources. In all sources, the different particle groups listed in the introduction, that is to say: lithogenic (dust, gravel production), biogenic (wood burning, agricultural activities, etc) and anthropogenic (the great majority) can easily be identified. DICTUC also mentions sources of gaseous pollutants (as mentioned in table 3), which will not be considered in this study as it will only focus on the breathable particles. But a general view of all pollution sources was necessary before focusing on PM.

The inventory of all emissions (gas, particles of all sizes) of atmospheric contaminants around Santiago was revised in 2005, in the framework of the Planning of Decontamination of Metropolitan Region (PPDA). This inventory was luckily done right at the same period as our study. Major sources in each category are listed below in 4 tables taken and simplified from "www.DICTUC.cl".



STATIONARY SOURCES

PUNCTUAL
- Combustion (G, PM)
- Evaporation (G)

DISSEMINATED
- Residential (G, PM)
- Commercial (G, PM)
- Forest fire (G, PM)

MOBILE SOURCES

ON ROAD
- Bus and Trucks (G, PM)
- Private and commercial vehicles (G, PM)
- Taxis (G, PM)
- Motorcycles (G, PM)

OFF ROAD
- Airports (G, PM)
- Agricultural and contractor machinery (G, PM)
- Bus terminals (G, PM)
- Railways network (PM)

TEMPORARY SOURCES

CONSTRUCTION / DEMOLITION
Buildings and Roads (PM)

RESUSPENDED DUST
Asphalted and dirt roads*

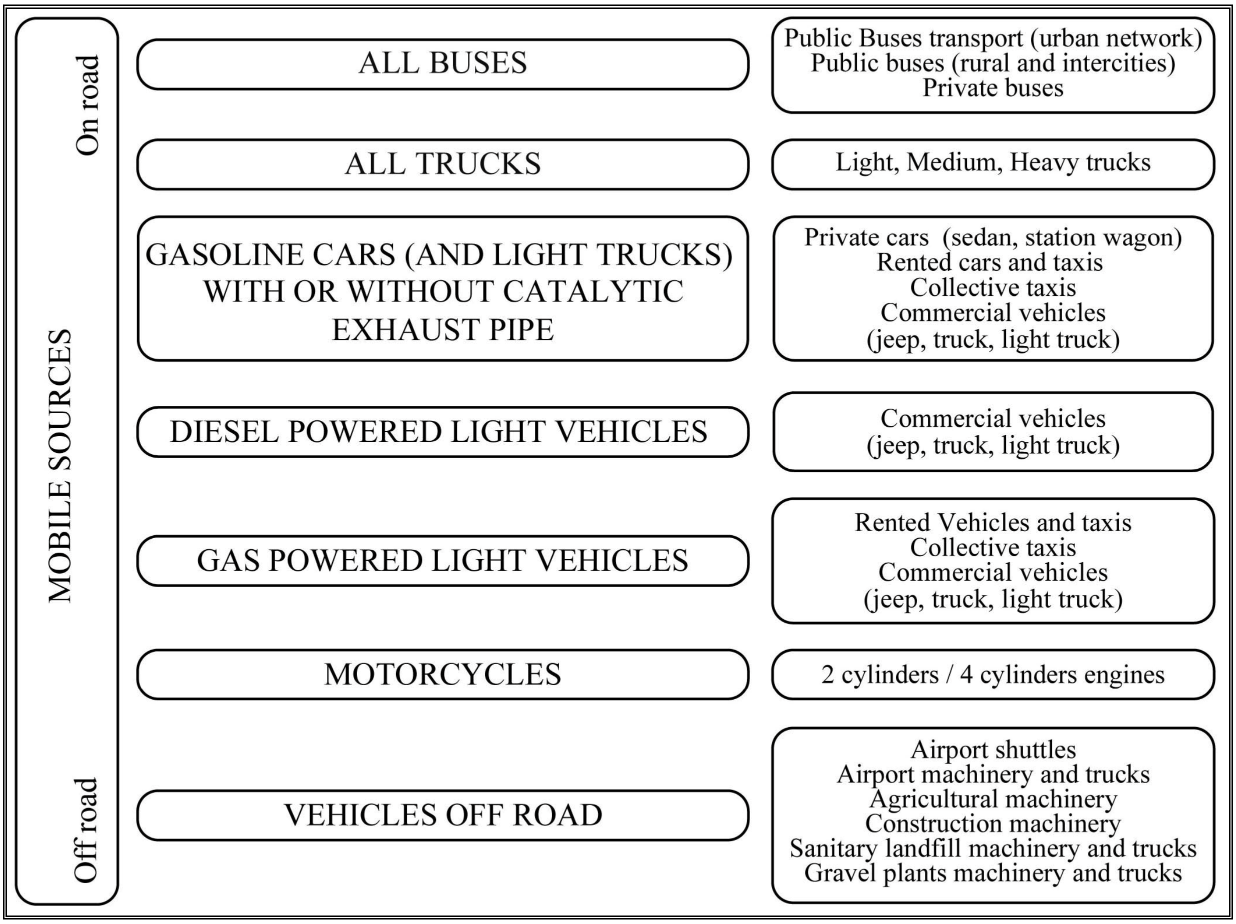
Table 3: Major contributors to fixed, mobile and temporary sources (from DICTUC, 2007)
G: emission of toxic gas; PM: emission of particles;
**: natural/lithogenic source (in opposition with all the others that are anthropogenic)*

Stationary Sources regroup sources with fixed locations either local or disseminated over a surface. Local sources are well identified and have well identified locations: a boiler, a power plant, whereas disseminated sources regroup punctual release points such as chimneys (residential or from small industries), exhausts from various small industrial companies (painting, repair shops) disseminated over the whole city, each being nearly negligible in the pollution budget but all of them contributing significantly to this budget. Stationary sources are listed below in table 4.

STATIONARY SOURCES	INDUSTRY (punctual/disseminated)	Power plants Industrial boilers Central heating systems Waste Incinerators Electricity-generators Production of: Iron and steel, copper and bronze , zinc, aluminum, lead Surface treatments Cement, lime and plaster production Fused glass production and Brick and ceramic production Asphalt production Asbestos production Chemical industry Manufacture of tires Paper production and recycling Grain Processing Bakeries Food manufacture LPG Production and packaging Fabrics printing and dyeing
	WOOD BURNING	residential heating**
	OTHERS RESIDENTIAL USES	Residential combustion of: LPG, GP, natural gas , kerosene Private use of solvents Building painting Glues, adhesives Residential production of NH3 Residential leaks of LPG
	VOLATILES	Distribution of fuels Laundries Vehicle Painting Industrial surface covering Application of asphalts Commercial leaks of Liquefied Petroleum Gas
	AGRICULTURAL BURNING	authorized and illegal agricultural burning**
	OTHER DISSEMINATED SOURCES	Forest and urban fires Cigarettes Production of handcrafted bricks Biogenic** (vegetable species) Fertilizers and pesticides Upbringing animal** Sanitary landfills** Used water treatment plants**

Table 4: Lists of stationary sources. Taken from DICTUC, 2007.
***biogenic sources*

Mobile sources (table 5) could either follow the road network or be outside of it and are listed below (from DICTUC). They are, per definition, all anthropogenic sources.



MOBILE SOURCES

On road	ALL BUSES	Public Buses transport (urban network) Public buses (rural and intercities) Private buses
	ALL TRUCKS	Light, Medium, Heavy trucks
	GASOLINE CARS (AND LIGHT TRUCKS) WITH OR WITHOUT CATALYTIC EXHAUST PIPE	Private cars (sedan, station wagon) Rented cars and taxis Collective taxis Commercial vehicles (jeep, truck, light truck)
	DIESEL POWERED LIGHT VEHICLES	Commercial vehicles (jeep, truck, light truck)
	GAS POWERED LIGHT VEHICLES	Rented Vehicles and taxis Collective taxis Commercial vehicles (jeep, truck, light truck)
	MOTORCYCLES	2 cylinders / 4 cylinders engines
Off road	VEHICLES OFF ROAD	Airport shuttles Airport machinery and trucks Agricultural machinery Construction machinery Sanitary landfill machinery and trucks Gravel plants machinery and trucks

Table 5: Lists of mobile sources. Taken from DICTUC, 2007.

The **temporary sources** belong to two groups, the first one is linked to construction and destruction of building, roads, bridges, etc. Dust so generated will come from building (and road) materials such as concrete, asphalt, asbestos (anthropogenic sources), but also from the soils nearby (natural/lithogenic sources). The second group deals with all processes which tend to induce natural dust re suspension, either from roads and street (anthropogenic/lithogenic) of from the soils through agricultural activity (lithogenic/biogenic). Such sources are listed below in table 6.

TEMPORARY SOURCES	CONSTRUCTION AND DEMOLITION	Building construction Road constructions Gravel production*
	RE SUSPENDED DUST	Paved street sweeping and cleaning program* Dirt road* Gravel roads*
	AGRICULTURAL LAND PROCESSING	Small farm activity** Industrial crops** Vegetables and fruit growing**

Table 6: Lists of temporary sources. Simplified from DICTUC, 2007.
**: lithogenic source*

Table 7 and figure 10, also taken from this report, are displayed in order to quantify the respective influences of the different sources for particles. They show their total emissions and the percentage contribution of the different categories.

The principal contributions for PM10 and PM2.5 are stationary sources with 2937.1 ton/year and 2437.7 ton/year, respectively (table 7). Industrial activities represent ~30% of this source (fig 9). The principal temporary sources contributions (table 8) to particulate matter are, in decreasing order: re suspended dust (91.3% (PM10) and 95.2% (PM2.5), construction and demolition (1.5% and 7.6 % for coarse and fine fraction respectively) then agricultural land processing (1% (PM 10) to 3% (PM 2.5)). This is in agreement with the observations previously made by Artaxo et al, (1999) and Morata et al., (2008) who mention re suspended soil and traffic emissions as the main aerosols particle sources.

2005 Annual inventory of emission, Metropolitan Region							
Stationary and mobile sources							
Category of sources	PM10 ton/year	PM 2,5 ton/year	CO ton/year	NOx ton/year	COV ton /year	SOx ton/year	NH3 ton/year
Industry	1266,9	994	7744,5	12332,1	7541,6	12829,3	217,4
Residential wood Combustion	693,1	673,6	8235	84,8	7465,6	11,8	71
Other Residential sources	78,9	69,6	338,3	1160,9	41241,6	294,2	3800,4
Commercial	0	0	0	0	7910,6	0	0
Agricultural burning	246,54	234,75	2139,19	101,55	171,4	11,73	11,54
Others	651,5	465,8	5249	135,9	18608,7	0	27724,9
Total stationary sources	2937,1	2437,7	23706	13815,2	82939,6	13146,9	31825,2
Public buses	221,4	196	1436,6	5866,7	714,6	21,6	1,9
Other buses	94,9	82,1	515,1	2507,3	235,2	9,2	1,2
Trucks	763,2	670,6	3514,8	11179,5	2199,3	43,5	6,5
Light vehicles (w. catalytic)	189,9	0	64837,9	10152,7	5524,8	50,8	1002,3
Light vehicles (w.out catalytic)	40,1	0	107269,3	7249,5	8943,3	11,8	6
diesel light vehicles	282,8	248,9	1167,2	948,8	218,1	7	0,9
gas light vehicles	1,7	0	949,9	71,5	105,6	0	NE
Motorcycles	1,8	0	3971,4	24,6	706,5	0,4	0,3
Off road vehicles	154,5	142	2215,2	973,3	320,3	45,5	31,6
Total mobile sources	1750,3	1339,7	185877,4	38973,8	18967,7	189,8	1050,7
Total mobile and stationary sources	4687,4	3777,4	209583,4	52788,9	101907,3	13336,7	32875,9

Table 7: 2005 Annual inventory of stationary and mobile emission, Metropolitan Region, (from CONAMA-DICTUC, 2007).

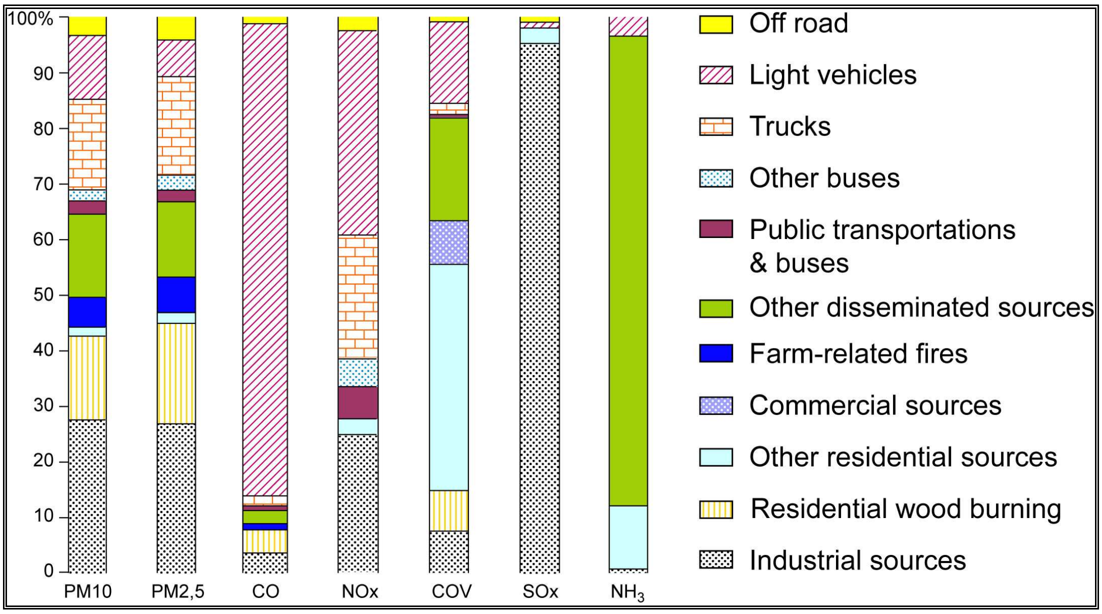


Figure 10: Contribution (in %) of main fixed categories of sources.

2005 Annual inventory of emission, Metropolitan Region			
Temporary Sources			
Category of sources	PTS ton/year	PM10 ton/year	PM 2,5 ton/year
Building construction	2362,5	1157,8	47,2
Road construction	85,6	55,5	1,3
Gravel production	1067	380,9	
Total construction and demolition	3515	1594,2	48,5
Paved street/road	75407,9	14560,5	2073,7
Dirt Street /road	16861,1	4608,4	681,2
Total re suspended dust	92269	19168,9	2754,9
Small farm activities	116,4	85	34,9
Industrial crops	0,2	0,2	0,1
vegetables	163	119	48,9
Fruit growing	27,4	20	8,2
Total agricultural land processing	307,1	224,2	92
Total temporary sources	96091,2	20987,3	2895,5

Table 8: 2005 annual inventory of temporary emission, Metropolitan Region (from DICTUC, 2007).

1.8 Location of the major industrial and mining activities and major roads around and within Santiago

1.8.1 Major industrial centers and roads

All along its development, the town has hosted many small/medium size industries and workshops. Then, from 1989 and latter emerged news industrials clusters. The most important one developed north of Santiago, close to the Panamerican highway and Santiago International Airport (fig 11). All the others are located west of the town, on flat (agricultural) lands, easy to construct (fig 11).

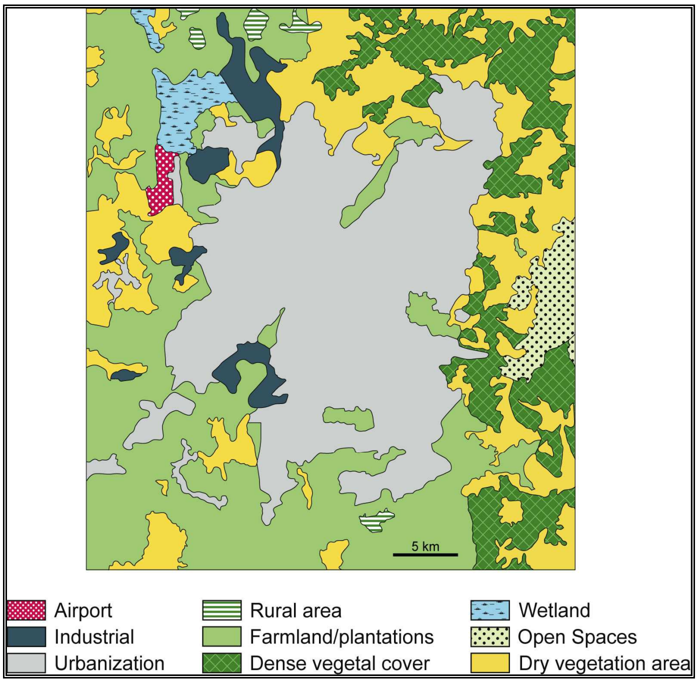


Figure 11: Location of the major industrial areas, the urbanized areas and the different vegetation covers. Vegetation cover, north, west and south of Santiago is mostly agricultural land. The eastern part, more rugged, has a either a dense (trees+grass) cover or nearly bare soil, in function of the altitude.

In the last ten years, the highway and major avenues network developed together with the city, ending with the scheme depicted in figure 12. The recently completed Americo Vespucio Avenue is a circular highway which connects all major radial avenues of the metropolis. Main ones are: a) the N-S Panamerican highway, b) the SW-NE Av .Bernardo O'Higgings – Providencia – Av. Las Condes urban highway, a 2x5 lanes avenue cutting the center of Santiago and used by ~50 bus lines and c) other major avenues such as Av Grecia, (fig 12).

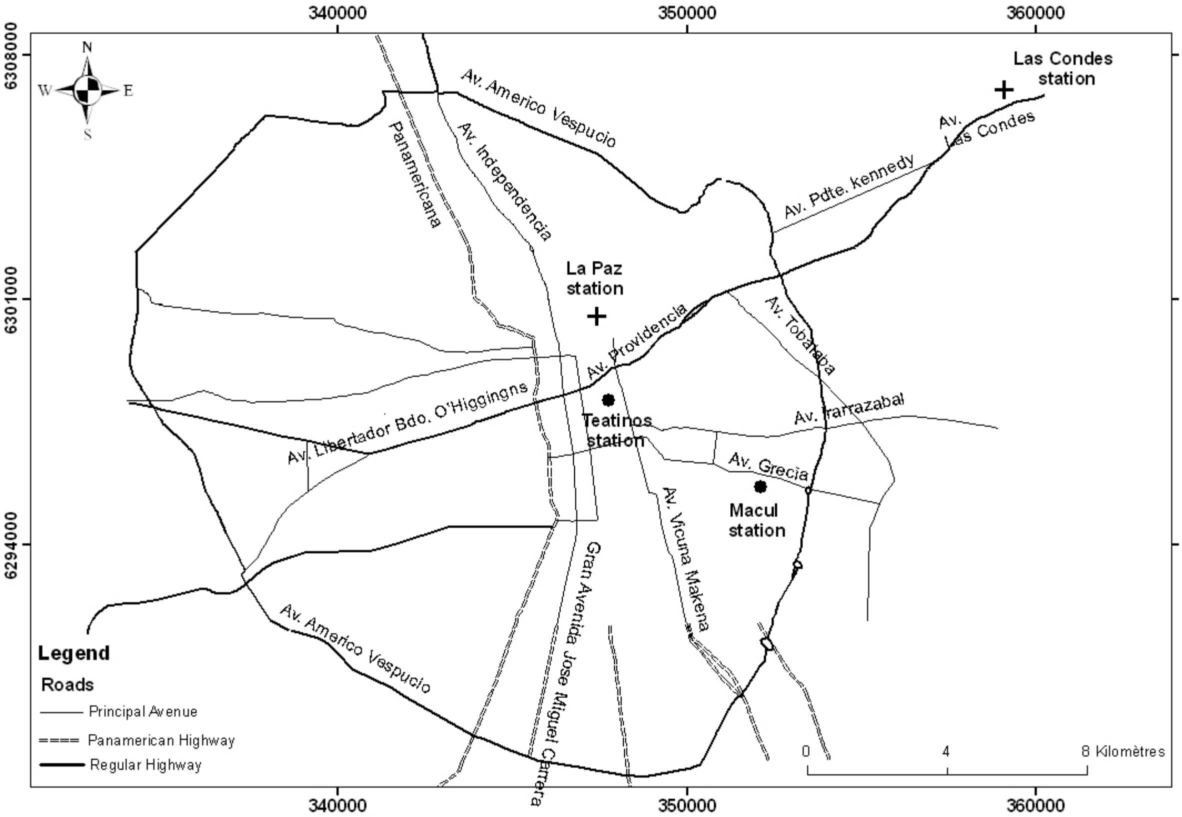


Figure 12: Principal highways and avenues in Santiago, with mention of the four stations studied here (modified from geological map of Sernageomin, 1999, 1:100000).
+: stations from the MACAM network. ●: stations set up by the University of Chile.

1.8.2 Major mining and smelting facilities

Refined copper production from the central region during 2004/5 was: Teniente mine - 437,393 tons of Cu and 5,249 tons of Mo; Andina mine - 248,137 tons of Cu and 3,244 tons of Mo (www.codelco.com); El Soldado mine - 66,480 tons of Cu; Chagres (copper smelter) - 138,063 tons; Los Bronces mine - 227,268 tons of Cu and 2,123 tons of Mo (annual report 2005 Anglo American Chile).

The major-mine related centers have to be considered as they may play a key role in the pollution budget, even if they are located 100 – 200 km far from Santiago.

El Teniente copper mine and its smelter plant, Caletones, (fig 1) is already known as a major source of air contamination in the region. Indeed it has been detected at La Leonera, 13 km south of the smelter, that S, Cu, Zn and As were quite enriched in particulate matter during working days when compared to strike periods (Romo-Kroger et al., 1994). In 1994

Caletones area was declared zone of saturation of SO_2 and particulate matter and, 4 years later, a decontamination plan started. Despite this initiative, the role of Caletones smelter emissions was pointed out in order to explain the large amounts of As, Cu and Zn found in aerosols from Linares, 230 km south of Caletones (Hedberg et al., 2005).

The Andina is an underground mine and Los Bronces an open-pit (SurSur). Both mines have a molybdenum floatation plant but Los Bronces also uses a sulfide treatment plant.

Ventana and Chagres industrial facilities (fig 1), 140 km north of Santiago, including copper smelters, are known as As, Cu and Mo emitters, with specific emission of Bi in Chagres and Ag, Pb and S in Ventanas (Hedberg et al., 2005). These two smelters are fed by the mines located in the Andes (Andina, El Teniente) (fig 1)

Numerous metallic ores, principally gold and copper deposits (fig 3) outcrop in the eastern border of Coastal Mountains, some of them displaying witness of past mining activity. Their associated wastes disposals might contribute to the breathable particles collected in Santiago.

1.8.3. Quarries, cement and plaster industries

Outcrops of non metal resources and industrial rocks such as limestone are found in the Las Chilcas (Kilc) and Lo Prado Formations (Kilp) (fig 3) and they are used for cement fabrication in Polpaico Hill (30 km NNW of Santiago) and at La Plata Gully, 50 km north of Santiago center.

Andesites belonging to the Lo Valle (Kslv) and Abanico formations (Olma) (fig 3) are extracted for ornamental uses at Colina Hill, (east of Chacabuco Mountains), Las Canteras, Conchali Hills and San Cristobal Hill. The Pudahuel ignimbrite (Qip), 10 km west of Santiago, is an important source for puzzolane and hosts many quarries. The fluvial and alluvial deposits that form Santiago basin are severely exploited as sources of sands and gravels for construction activities. Associated to lake deposits, clay minerals are exploited for brick fabrication at Huechuraba and Batuco, 35 km north of Santiago.

1.8.4. Other major industries

The recently developed industrial areas (fig 11) have been already mentioned. But industrial activity is also densely and homogeneously spread over the city. The most important plants/factories/industries, specially those close to the 4 stations studied here, are displayed on figure 13. They are boilers (industrial or heaters), ovens (industrial or bakery), power plants, power generators, crematorium, paint factories and painting workshops, dry cleaning etc. The more numerous are the power generators, homogeneously distributed over Santiago, as any important building, any industry, any hospital is so equipped in prevention of the frequent power failures.

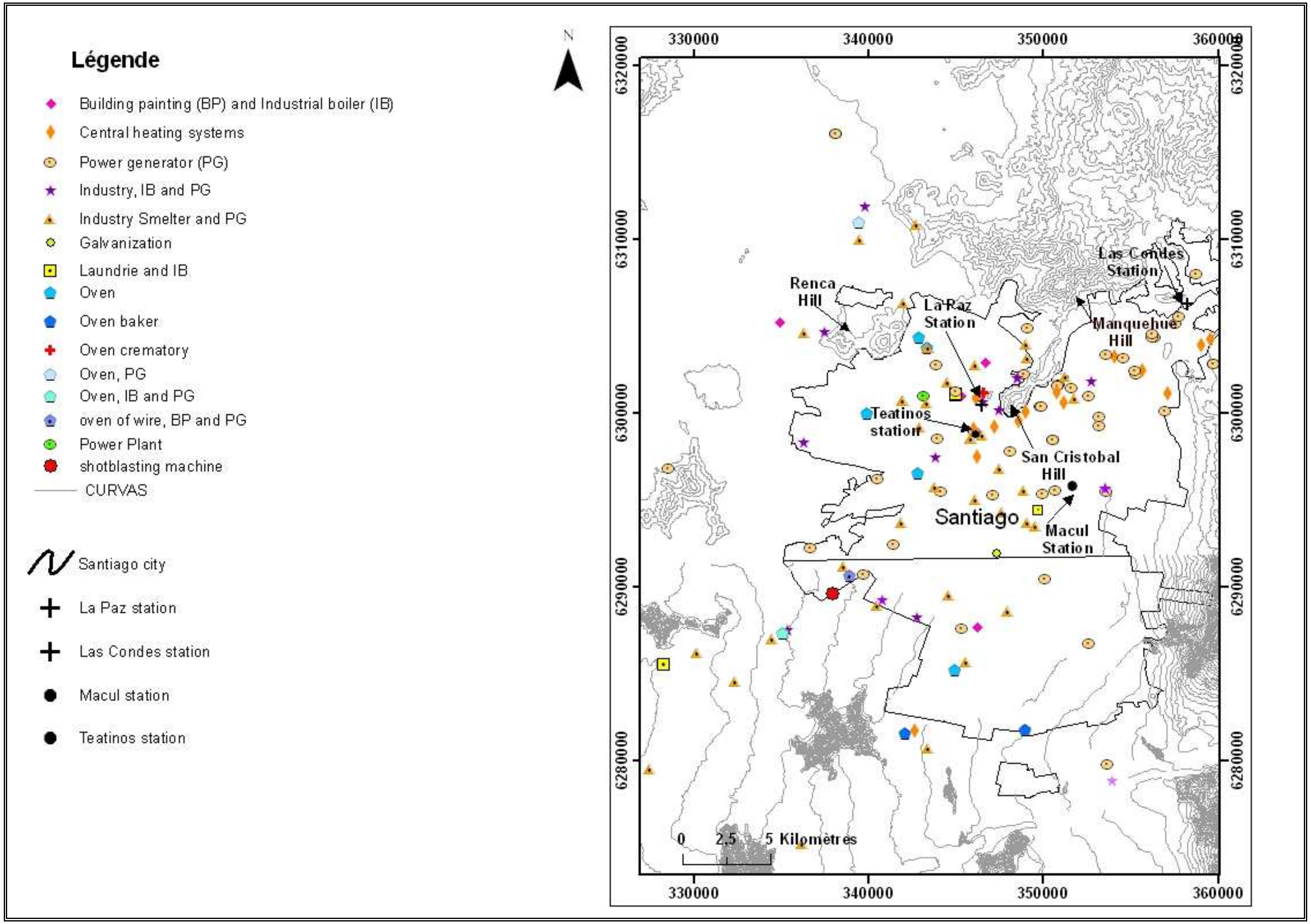


Figure 13: Type and location of the main potential pollution sources scattered within Santiago de Chile (topographical map from Sernageomin,1999. 1:100000)

1.9 The government survey program and the effect of the last regulations.

Since the mid eighties, the Ministry of Health has implemented a national network in order to control air quality. This network first monitored PM10 and pollutants like CO, SO_2, NO_2, O_3 then a few years later PM2.5 and lead were added to the list. In the early nineties, new cars were required to have catalytic converters, standard emissions were fixed for industrial and non industrial pollution sources as well as for residential heating, and an emission trading program was set up (Koutrakis et al., 2005). In 1996 Santiago de Chile was declared zone of saturation for ozone, breathable particulate matter (size $< 10\mu m$), particles in suspension and carbon monoxide, and latent zone for nitrogen dioxide with the subsequent creation of the decontamination plan of Santiago (PPDA) (Lents et al., 2006).

Mobile sources contribution to PM2.5 budget has doubled in the last 10 years, whereas stationary sources contribution to the same budget has been reduced by half of its level in the early 1990s (Jorquera et al., 2002). Indeed in 2007 the vehicle availability reached a total of 1.200.000 units, so rules were set which reduced both the number of vehicles and their individual pollution level. As an example, through the TranSantiago program launched in 2007, the fleet of buses which counted 13.000 units at the beginning of the 90s, was reduced to 8000 buses nowadays (retrospective Analysis 1997-2007) and old buses were forbidden (Jorquera et al., 2002).

Pb, Br and S concentrations in PM2.5 decrease in Santiago from 1998 to 2003 (Sax, et al., 2007) as a consequence of the elimination of leaded gasoline in 2001. Then the desulfurization of diesel and petroleum was decided in 2004 with a maximum authorized level of 50 ppm and 30 ppm of sulphur, respectively (Retrospective Analysis 1997-2007).

Infortunately, since 2004, Argentine gas exports to Chile have fluctuated between 20-50 percent below the volumes fixed by contract between the two countries, with natural gas supplies ceasing completely for a brief time during the bitter winters of 2006 and 2007 (Speicer R, 2007). Natural gas supply was replaced by liquefied petroleum gas (LPG) and the more pollutant diesel oil. In this period also the indoor heating has changed. Wood, which had been banned by law, has been replaced by kerosene, (natural gas) and oil.

Because of all these past changes in pollution regulation, and in order to evaluate the ones taken fairly recently, it was time to set up an in depth geochemical study of the pollution carried by breathable particles, especially with respect to their toxic metals loads. We choose to work on 2004-2005 samples which could be compared to previous studies and could be used in further studies in order to quantify, among other points, the benefits of all the drastic decisions taken.

1.10 Previous studies performed on PM 10 and PM 2.5 fractions from Santiago

In general, the studies related with PM at Santiago, describe their concentration tendencies, seasonal variability and their behavior with respect to the meteorological parameters (Gramsch et al, 2004; CENMA, 2009). Other parameters of the PM10 and PM2.5 have also been studied. For example, Gramsch et al. (2004) monitored elemental carbon and PM2.5 concentrations. Magnetic susceptibility was determined and compared with chemical composition of aerosol in Santiago (Silva, 2005). Also, specific dispersion models for the distribution of SO_2 within Santiago Basin were proposed by Olivares et al. (2002) and Gallardo et al. (2002) and its impact in the agriculture was evaluated by Garcia-Huidobro et al. (2001).

This review will focus on PM concentrations, mineralogy and metal concentrations, which are the main point of this specific study.

1.10.1 Concentrations (µg/m^3 air) in PM10 and PM2.5

Studies in the last 10 years have shown a progressive reduction in concentrations in PM10 (fig 14). Reduction percentage appears to be smaller for PM2.5 than for PM10 (41.8 µg/m^3 in 1998-1999 to 35.4 µg/m^3 in 2002-2003 (Sax et al., 2007). High seasonal variability was observed in PM2.5, while the pattern observed in PM 10 was similar between warm and cold seasons (Koutrakis, et al., 2005). This decreasing tendency cannot be explained by meteorological factors, but is to be linked to a decrease of PM emissions.

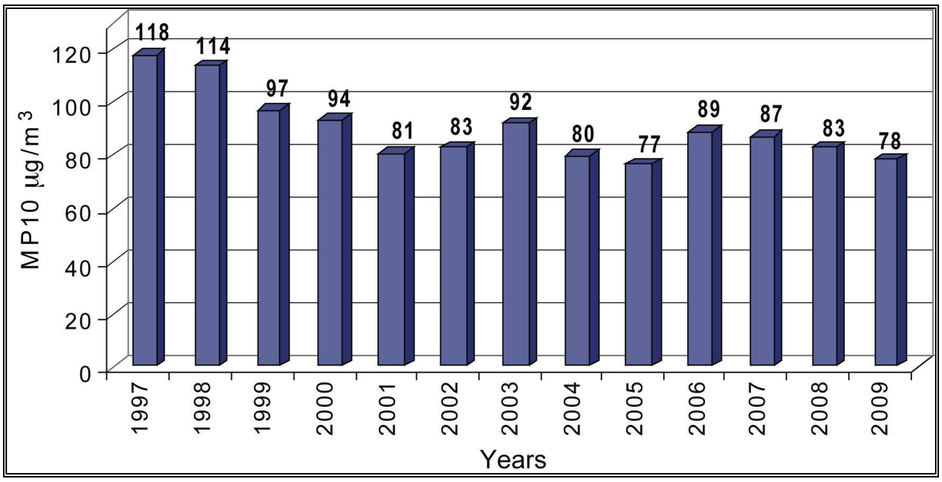


Figure 14: Average concentrations of PM10 from April 1 to September 17 of 1997 to 2009 (from CENMA, 2009).

1.10.2 Mineralogy

The first study done on the physical aspect (diameter, shape) and mineralogy of the particles was done by Préndez, (1993). The author combined SEM and electronic microwaves methods on particles collected with an Anderson Impactor at Cerro San Cristobal, 30m above the surface. The samples collected during the morning showed a relation between 3 µm size particles and spheric shape; while most particles between 1.4 and 2µm displayed irregular shapes. In addition, the authors observed a relation between irregular forms and elements with crustal origin (Al, Si, K, Ca, Fe, Mn). In the morning, spheric particles are associated with Si, Fe, S, Cl, Zn, Ti, which, the author assumed, could come from incinerators while they associate irregular forms, found in the afternoon, with fuel combustion and incineration. During the afternoon, large agglomerated particles (2-3um) were less numerous than in the morning aerosols, while the number of spheric and regular shaped particles increased. These characteristics are an evidence for gas to particle transformations during the day and also for secondary particle formations, as also demonstrated by Gramsch et al. (2009).

Silva, (2005), used magnetic susceptibility on 2004 aerosols from Santiago. They could identify specific ferromagnetic phases. Positive and negative signals of magnetic susceptibility were observed in coarse (> 8µm) and fine fractions (0.4 – 8µm), respectively. These signals were related to mafic compositions of the coarse fraction, with dominant Fe and Ti, while Si and Al were dominant in the fine fraction. In both fractions, magnetite was recognized as a principal iron oxide phase.

Morata et al., 2008 studied a few filters collected in 2004 in two sites (fig 12) with PIXE and SEM techniques. Lithogenic particles such as pyroxene, amphibole, plagioclase and feldspar were recognized, their origin supposedly related to all the volcanic and volcano sedimentary formations present around Santiago. These particles were better represented in the PM10 fraction than in the 2.5 ones. Particles with clear anthropogenic signature were also identified, the occurrence being more important in the PM2.5 than in the PM10 fraction. Potential sources were proposed for these particles, as developed in Chapter 3.

1.10.3 Metal concentrations and source identification.

These previous studies used PIXE, ICP-MS, XRF and SEM techniques in order to quantify elemental concentrations in the PM, then proposed relations with potential sources. We present here their results, the potential sources invoked (and their elemental signature), following the sources classification proposed by DICTUC, 2007.

1.10.3.1 Stationary source

Oil and coal combustion (Power or Industrial plants, central heating systems)

Préndez, (1993) was able to identify spheric particles, black and white, composed of Na, A1, S, Si, C1, Ca, Fe, V and associated this to oil combustion.

Artaxo et al. (1999) identified residual oil combustion and /or industrial emissions with V, Ni, Zn, Mn and Cl. Arsenic and sulfur emission has been considered independent of sulfate source. The latter has been related to S, Se, K and P and this source included secondary aerosol formation from oxidation of SO_2, with the observation being consistent with Morata et al. (2008).

Moreno et al. (2010) using XRF on PM 2.5 from aerosol samples collected between 1998 and 2007, identified oil sources and correlate them with Mn, Cu, Fe and Zn.

V and Ni are widely associated with oil combustion (Celis et al., 2004; Pey et al., 2009) while Cr is associated with coal combustion (Hedberg et al., 2005).

Incineration Processes

Préndez, (1993) related Na, Al, S, Cl, K and Ca with incineration processes.

Copper smelter

As previously mentioned, two major copper mines: Teniente and Andina and their associated smelters: Caletones; Ventanas and Chagres are less than 200km far from Santiago. To determine their impact on the air quality of Santiago, we considered the previous work in this region.

Romo-Kroger et al. (1994) used Particle induced X-ray emission (PIXE) on the aerosols taken from La Leonera, and recognized Caletones as a major source of air contamination. The copper smelter is related to S, Cu, Zn and As.

Artaxo et al. (1999) studied (with PIXE) the aerosols compositions from Santiago and their sources apportionment. Copper emissions could be responsible for As and Cu.

Kavouras et al. (2001) used X-ray fluorescence (XRF) on PM2.5 and PM10 fractions collected in five cities of Chile. According to this study, Cu, As and Zn concentrations were much higher in Rancagua, Valparaiso and Viña del Mar (fig 1) than those measured in Temuco (617km south of Santiago) and Iquique (1460 km north of Santiago). This shows that the central chile are most impacted by copper smelting than southern Chile.

Gidhagen et al. (2002) using an ICP-MS, detected high arsenic concentrations (up to 30.7 $ng/m^{3.}$) in PM10 sample from seven rural stations in Central and Northern Chile, located tens to hundred of kilometers far from the nearest copper or gold smelter.

Hedberg et al. (2005) used an ICP-MS, in order to identify the principal contributions to PM 10 and arsenic concentrations in the Central Chile. They argue that Caletones smelter emissions are characterized by As, Cu and Zn, while Ventana and Chagres smelters emit As, Cu, Mo (and Bi in Chagres, Ag in Ventanas).

Sax et al. (2007) used XRF on the PM 2.5 aerosol filter samples from Santiago (MACAM network, Parque O'Higgins station). They determined that the trend in the elemental composition of PM 2.5 in Santiago from 1998 to 2003 shows a significant decrease of Pb, Br and S concentrations, probably due to the elimination of the leaded gasoline in 2001 and to the desulfurization of diesel and petroleum since 2004.

Finally as previously mentioned, Morata et al. (2008) proposed a relationship between S and copper smelter.

Residential sources (Residential combustion of: LPG, GP, natural gas, kerosene)

Ruiz et al. (2010) identify different indoor sources which have different geochemical signatures. Br, Cl, Cr, K, Na, Pb and Se are found in kerosene homes, whereas LPG home - atmospheres have in their composition Cl, K and Zn. Compressed natural gas (CNG) homes only show Cu and K, whereas in all homes there were indoor enrichments in Al, Ca, Cu, Mg and Ti.

1.10.3.2 Mobil Sources

Artaxo et al. (1999) define Br, Pb, BC, K and Sr as elements which characterize vehicular emissions.

Morata et al. (2008) characterized iron oxide particles and proposed for them a vehicular-traffic origin as put forward by Silva, (2005).

Sax et al. (2007) show a reduction in Pb, Br and S concentrations probably related to the street paving and cleaning programs or to the introduction of unleaded gasoline and low-S diesel.

Moreno et al. (2010) identified motor vehicle sources by Br, Cl, Pb and K.

1.10.3.3 Temporary Source

Natural origin

- Rojas et al. (1990); Ortiz et al. (1981) have associated Fe, Mg and Mn with natural origin.
- Préndez et al. (1984 and 1989), Ortiz et al. (1981) and Morales et al. (1983), affect a natural origin to the elements Na, Al, Ca, Sc and Si.
- Préndez, (1993) and Morata et al. (2008) recognized square crystals of Na and Cl (sea salt). Indeed, Na and Mg are currently used as tracers of sea sources (Hedberg et al., 2005; Kang et al., 2009).
- Artaxo et al. (1999) defined soils dust by the elements Ca, Si, Ti, Fe, Al and Sr
- Morata et al. (2008) consider that major elements Al, Ca, Na, Fe and Mg and some trace elements such as Zr, Ti, Sr and Rb are tracers of natural origin.
- Moreno et al. (2010), identified soil source with Al, Si, Ti and Ca in both fractions, and Fe, Ca and Mn in $PM_{2.5-10}$ fraction.

Wood combustion

Even if also considered as having a crustal origin, K is generally used as tracer of wood combustion (Carvacho et al., 2004; Celis et al., 2006; Morata et al., 2008).

Traffic or mobile source

- Moreno et al., 2010, identified S and P as tracers of combustion in diesel vehicles, generators and motors, even if these elements can also be related with copper smelter around of Santiago.

1.11 Conclusion

The urban expansion and the consequent industrial development produce a mixing of pollutants sources that impact Santiago, amplified by adverse meteorological conditions. Over the last 20 years important decisions have been taken in order to improve the quality of air in Santiago.

Different studies have been performed in Santiago in order to identify the patterns of PM10 and PM2.5. However, it is only in the last decade that started the studies dedicated to the identification of sources through their elemental concentrations. According to the works mentioned before (in metal concentrations), the major sources unambiguously identified in previous works in Santiago can be summarized as:

- Natural (lithogenic) sources regrouping soils or re suspended dust and sea salt,
- Mobile sources related with motor vehicle emissions,
- Industrial emission and oil combustion,
- Copper smelters (Chagres, Ventana and more specifically Caletones) have also been identified as pollution sources, even if located far from Santiago.

CHAPITRE 2: SITES, MATERIELS ET METHODES

2.1 Introduction

Le chapître 1 vient de présenter l'ensemble des facteurs climatiques, géologiques, météorologiques, topographiques et de végétation qui sont susceptibles de jouer un rôle dans la distribution et la concentration des polluants.

Mais il est évident que, en plus de ces facteurs physiques, d'autres facteurs, parfois d'influence plus locale, sont liés à l'activité humaine et à la concentration urbaine (émissions des industries, incinérateurs, trafic, etc. Il est important de mesurer quelles sont les différences (qualitativement et quantitativement) visibles entre sites soumis à ces derniers facteurs. En effet, dans le cadre des premiers programmes de réduction des niveaux de pollution, des études de minéralogie et de chimie ont été mises en place dès les années 1980 (Prendez 1993, Artaxo et al., 1999). Ces études ont montré qu'il y avait des secteurs plus affectés que d'autres par la pollution et que la concentration du matériel particule variait d'un endroit à l'autre.

Nous avons donc choisi de travailler sur 4 sites représentatifs présentant des environnements industriels et routiers différents, lesquels seront présentés en détail. Ainsi, deux sites ont été sélectionnés en centre ville, affectés par la pollution industrielle et le trafic (La Paz et Teatinos), et deux autres sites ont été sélectionnés dans des quartiers plutôt résidentiels, donc moins soumis à ces contaminations anthropiques (Macul et Las Condes).

Mais tout ce travail de caractérisation puis d'analyse chimique n'a de valeur que si les données sont fiables. Tous les protocoles de prélèvement, de manipulation et d'analyse sont donc donnés en détail, et permettent de quantifier la fiabilité et les limites des observations et analyses présentées ensuite.

2.2 Selection criteria for the four sites

Even if the industrial network is scattered over the metropolis, as are the main roads and highways, there are differences in the type of urbanization between districts. In order to check the influence of both local sources and effects on pollution levels, we have selected four stations. All four sites reflect fairly well Santiago diversity, as two are in residential areas while the two others are in densely populated areas. We could have chosen to study more stations, but this would have prevented us from checking with a statistically significant dataset the effect of the meteorological conditions on trace metal contents of the different fractions. Indeed this would induce the analysis of a too huge amount of samples. During a preliminary study dedicated principally to mineralogical observations, we have selected 6 filters collected at the stations Macul and Teatinos. For the main geochemical project we have chosen 2 other sites, La Paz and Las Condes (table 9 and fig 15), where complete time series of samples were available.

2.3 Description of the sites and their surroundings

The four chosen sites (see their location in figure 12 chapter 1) belong to two different networks. The Macul and Teatinos stations belong to the University of Chile and are run for pure research projects. The samples collected there in 2004 were used in a preliminary mineralogical study, published by Morata et al. in 2008.

The two other sites, La Paz and Las Condes are run by the MACAM (Monitory Quality of Air Network, belonging to Metropolitan Regional Ministerial Secretary) which surveys pollution levels in the air of Santiago and is in charge of public alerts. The MACAM network, has 8 stations with automatic and semiautomatic monitoring systems located in different places in Santiago. In all the stations, concentrations of carbon monoxide, sulphur dioxide and ozone, and the amount of breathable particulate material are measured systematically. In three of these stations, nitrogen oxides concentrations and physical parameters such as temperature, humidity, solar irradiation and wind direction are also measured. Data are stored in AIRVIRO data base, located on the National Centre of the Environmental Department (CENMA).

Monitoring station	Type of equipment	site	characterisation of sites
Teatinos	Gravimetric	Urban	Commercial/residential
Macul	Gravimetric	Urban	Residential
La Paz (F)	Gravimetric/TEOM	Urban	Commercial/residential
Las Condes (M)	Gravimetric/TEOM	Urban	Residential

Table 9: Compilation information of monitoring stations used in the present study

Figure 15: La Paz and Las Condes stations equipment (from Berrios et al., 2006, MACAM report).

2.3.1 Teatinos Station (run by Univ. of Chile)

The Teatinos street is a ~ 1km long canon street. It is located in the center of Santiago, 150 m far from Av. Libertador O'Higgings (fig 12, chapter 1), a five-lane and one of the most heavily used avenue of Santiago, lined by crowded sidewalks. Avenue Makena is also quite close (~ 700 m) to the station. This station is close (500 m) to the Moneda Palace (Presidential Palace) and to the major square of Santiago (Plaza de Armas), in an administrative district hosting ministries and banks. It is a commercial/offices area with a very low vegetation density and high cars and buses traffic. Industrial activities close to the site are reported in figure 16.

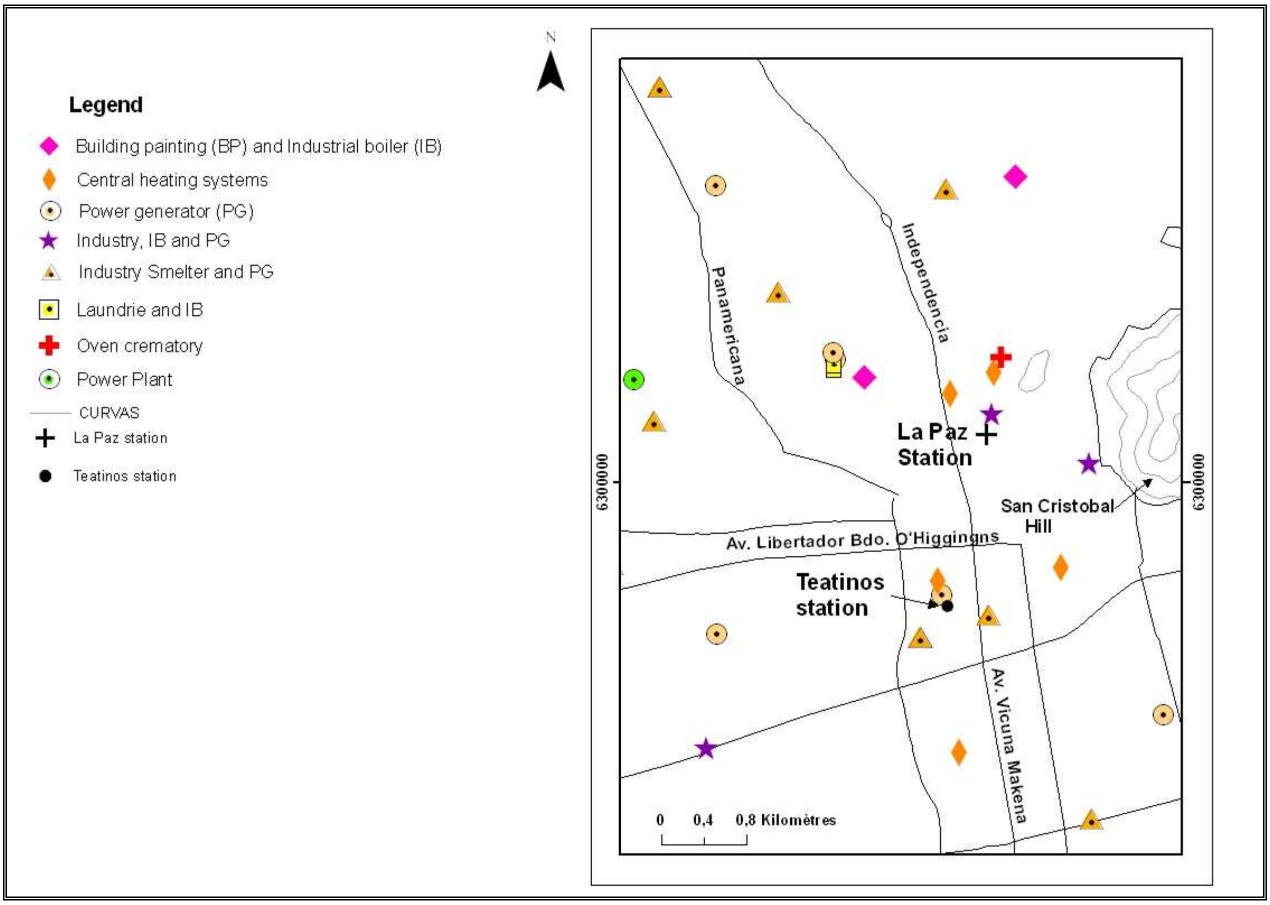


Figure 16: Principal sources of pollution that impact La Paz and Teatinos stations: powerplant, heating boiler of Hospital of Chile University, industrial contributors boiler and other minor contributors as dry cleaners and power generator. (topographical map from Sernageomin, 1999. 1:100000)

2.3.2 Macul Station (run by Univ. of Chile)

This station is set on the campus of the Faculty of Sciences of the University of Chile (fig 17), on the eastern part of the city, in a residential area with low building density and numerous trees, but fairly bare soil. It is 300 m away from two major roads (Av. Grecia and Macul) and 2 kilometers away from Vespucio Avenue, the Santiago ring highway (fig 17). Nearby potential pollution sources are reported on figure 17.

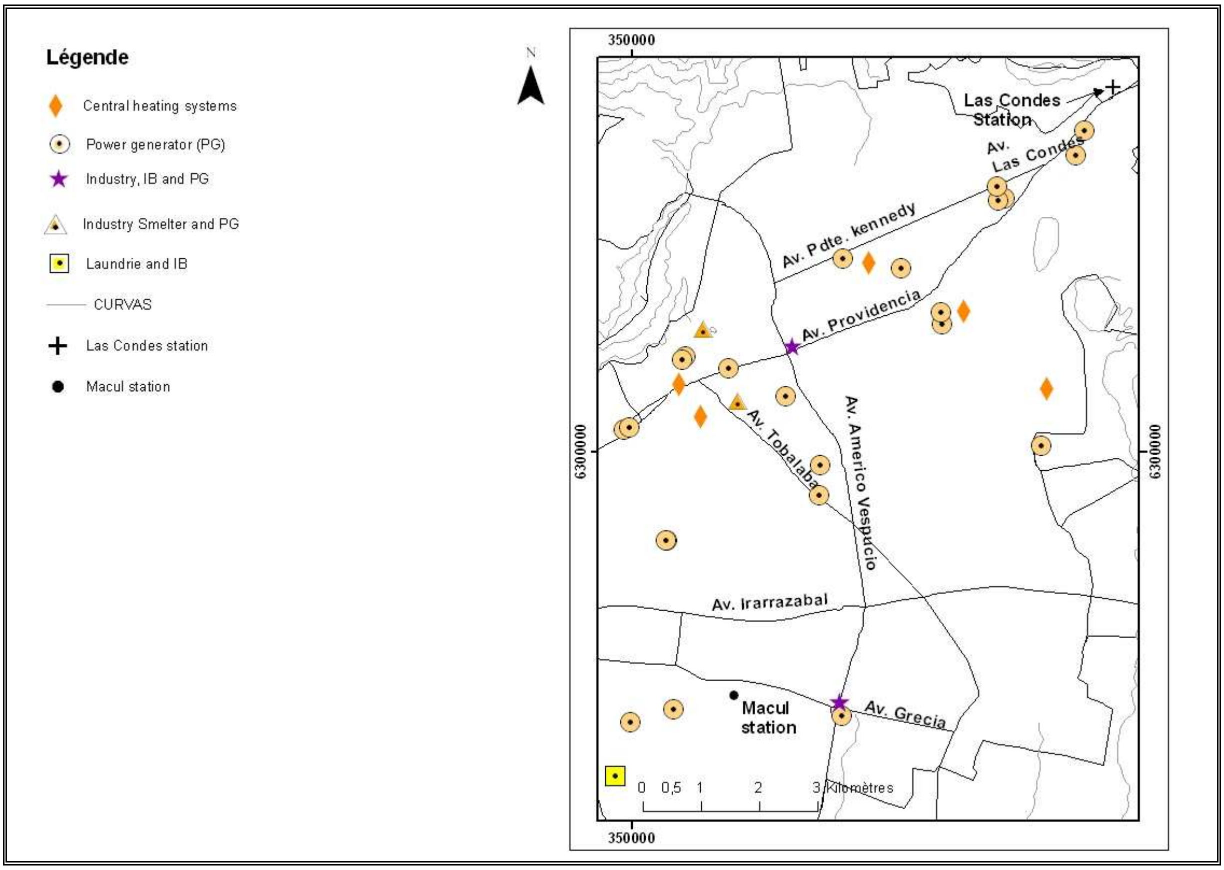


Figure 17: Principal sources of pollution close to Las Condes and Macul stations. (topographical map from Sernageomin, 1999. 1:100000)

2.3.3 La Paz station (part of the MACAM network)

The La Paz station is located in the central part of the city, 2 km north from the above mentioned Teatinos station, 1 km north of the Mapocho river and west of the San Cristobal Hill (fig 3 chapter 1), covered by scant vegetation. The surrounding is a mixed residential – commercial - industrial area, densely constructed (fig 16). With the exception of the General Cemetery (which hosts a crematory) and the Blanco Hill, the tree coverage of this area is very low. This district is also cut by three important traffic roads: Independencia, Santa Maria and Ismael Valdés. It also hosts building heaters: 2 for the University of Chile Hospital and one for the Psychiatric Institute. Figure 16 shows that industrial heaters are located approximately 1 km east of the station, while an industrial dry cleaner is plotted 1.5 km to the west. A painting workshop and many electric generators have also been identified. Finally, 3.5 km to the east there is an important electric power plant using alternatively coal or diesel.

2.3.4 Las Condes station part of the (MACAM network)

The Las Condes station is located at the east of the city (fig 17), on a gentle slope (Andean foothill), where the Mapocho river leaves the Cordillera and its valley becomes larger. The environment is residential and displays, unlike all other stations, a high tree coverage. Costanera Norte highway and Kennedy Avenue are the main avenues in this area. One of the biggest shopping centers in Santiago is approximately 3 kilometers west of the station. The main identified potential pollution sources are electric generators and heaters of residential buildings, health and educational centers and hospitals. The station Las Condes was selected because it could represent the global urban pollution, without the impact of clearly identified industrial pollution sources (fig 17).

2.4 Filter collection and sampling

2.4.1 Teatinos and Macul Filters

Teatinos

This station was equipped with a stacked filter unit (SFU). The sampler was placed on the top of an eight-floor building, about 30m above ground level. The samples were collected during a period of 12 weeks in winter 2004 (table 1 in chapter 3 in Morata et al. (2008)). Three samples per week were collected, each sampling lasting 24 hours. Seven samples (on Teflon filters) were collected during one month in July-August 2004. One critical day (ICAP pollution level 244 $\mu g/m^3$ (PM10) as defined table 1 chapter 1) was selected through S_2F_1 (17/07/2004) sampling.

Macul

The sampling was done with a double PM10-PM2.5 collector, which was placed 2m above ground level. Typical collection rates were around 18 l/min. The filters here were either Teflon or polycarbonate both utilized in SEM analysis. This sampling was performed for one week in June 2004, during which 10 samples were obtained.

For both sampling, filters were weighted before and after sampling with a ±0.001 mg microbalance in order to measure the amount of collected particulate matter (table 1 in chapter 3 in Morata et al. (2008)). Then they were stored in sterile Petri dishes in temperature- and humidity- regulated chambers.

2.4.2 La Paz and Las Condes filters (MACAM network)

Filters were collected with a Manual Dichotomus Sampler "Sierra-Andersen 240”. It is a semiautomatic, programmable (fig 18) sampler of low volume (Berrios et al., 2006). This equipment allows simultaneous collection of both PM2.5 and PM10 fractions. The design of the inlet allows only particles smaller than 10 microns to enter the sampler, where they are separated into two size fractions and collected on two Teflon filters (Pall Flex; Berrios et al., 2006), the fraction named PM10 regrouping all particles between 2.5 and 10 µm and the PM2.5 fraction only particles under 2.5 µm. The PM10 fraction receiver tube has a flow rate of 1.67 liter per minute while the PM2.5 receiver tube has a flow of 15 liter per minute.

Each year, sampling is done every day from April to September, every two days in October, November and March and every three days from December to February. Indeed, pollution peaks are in winter (April to September) while the rest of the year suffers less pollution. Sampling is performed between 10:00 to 10:00 the next day in autumn and winter and between 00:00 to 00:00 in spring and summer.

Filters are weighed before and after sampling, using a ±0.001 mg microbalance and stored in individual plastic boxes in dry chambers (fig 19) which provide a 50% controlled relative humidity and temperature between 20°C and 25°C (tables 2 and 3 in chapter 4).

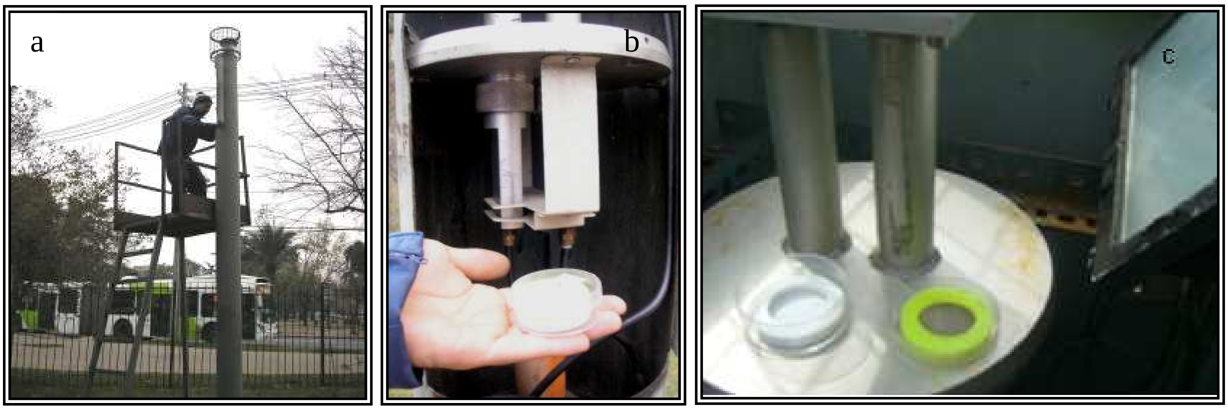


Figure 18: (a) Dichotomus sampler and installation of filter in the field by MACAM network technician. (b and c) Filter fot fractions PM10 and PM2.5.

Figure 19: Gravimetric laboratory equipment from the air quality monitoring network, (from Departamento de Salud Publica sanitaria de Ministerio de Salud Region Metropolitan / Department of Public Health, Metropolitan Region).

2.5 Analytical techniques

The techniques used in the project are: electron microscope (SEM) for the mineralogical identification, PIXE and ICP-MS for major and trace elements analysis. These techniques were, as much as possible, applied jointly to the same sample, for chemistry and mineralogy correlations and sources identification. In order to avoid any contamination problem, all the filters we studied were manipulated in class 1000 clean rooms. First, photos were taken of all filters, which were then weighted with our own balance. In order to cut the filters easily and without any pollution, an -all Teflon- special device was made which allowed cutting the filters in perfect quarters with a ceramic knife, without touching the filters (fig 20). All tools (tweezers, knive, etc) were also made of Teflon and carefully cleaned (MilliQ water, diluted HCl bath) between each filter processing.

2.5.1 SEM analysis

They were performed using two different equipments from two laboratories. The first analyses were performed with a JEOL JSM 5900 LV-SEM at the “Universidad Catolica del Norte (Antofagasta, Chile) while the others were done with an all automated JEOL JSM 6360 LV-SEM at the LMTG, University Toulouse III.

2.5.1.1 Sample preparation

Polycarbonate filters were studied in Antofagasta, where different tests have been performed in order to determine the best conductive cover: carbon or gold. We tested also analysis without any cover, as the filters were generally covered by carbon nanoparticles issued by vehicles exhaust pipes. Imaging quality and signal stability were poor on these non covered filters whereas both carbon and gold covers allowed good observations and imaging conditions. Thus a small piece of a filter was cut and glued with doubled sided tape on an aluminum handle, and a thin carbon cover was applied. The Teflon filters from the MACAM network were studied in Toulouse. They were prepared and mounted the same way.

2.5.1.2 Data acquisition and processing

The two SEM used in this study were coupled with an energy-dispersive X-ray microanalysis system (SEM– EDX). The first data in Antofagasta were acquired “manually”: grains on the filters were selected and their EDS spectra analyzed for further identification. This method is biased for two reasons: first the analyst is more attracted by grains with striking shapes than by plain irregular ones, second, data are not statistically valid as this method being time consuming, only a few tens of grains are analyzed. Data at LMTG were collected semi – automatically: all grains with size ≥ 1 micron were selected on a (~400 mm^2) surface of the filter. Then EDS spectra were analyzed automatically. This second method prevents from the two above mentioned biases. These spectra were obtained on the two types of filter: polycarbonate and Teflon. Both contain chemical components that could interfere with the particles spectra and bias the interpretation. Therefore clean filters were first analyzed in order to obtain their chemical spectrum. Polycarbonate filters have a very smooth surface in which particles appear clearly, whereas on the Teflon filters the fibrous surface could sometimes cause confusion between very small particles and globules from the Teflon lattice. Moreover, Teflon filters always provide C and F peaks that can disturb the EDS spectrum of very small grains (~ 1µm) whereas polycarbonate filters only contribute to the C peak.

Presence and signal intensity for the following chemical components were checked in each individual grain: Si, Al, Ca, Na, Mg, K, Fe, S, Cl, Ti, Ba, Cu, Zn, Mn, Pb, (O, C). From this information, in most cases, hypothesis could be made on the mineralogical nature of most grains. In some cases mineralogical determination was quite sound and precise: large (6-10µm) well crystalized flat crystals would provide spectra very close to the standard ones for a given mineralogical species. But in other cases only a very general mineralogical group could be proposed from the EDS spectrum, either because of mixed grains, size of the grain or position on the filter. In any case, biogenic grains were recognized without ambiguity while sometimes, grain nature and origin (geological, anthropogenic or atmospheric) were impossible to decipher.

2.5.2 Proton-induced X-ray emission (PIXE) analysis

Analyses were performed at the Physics Department of Chile University using a 2.2 MeV protons flux produced by a KN3750 Van de Graaff electrostatic accelerator.

2.5.2.1 Sample preparation

The polycarbonate filters which were analyzed by PIXE did not need any preparation or cutting. Analyse was performed on a 1.5 mm diameter zone, for statistical reliability.

2.5.2.2 Data acquisition and processing

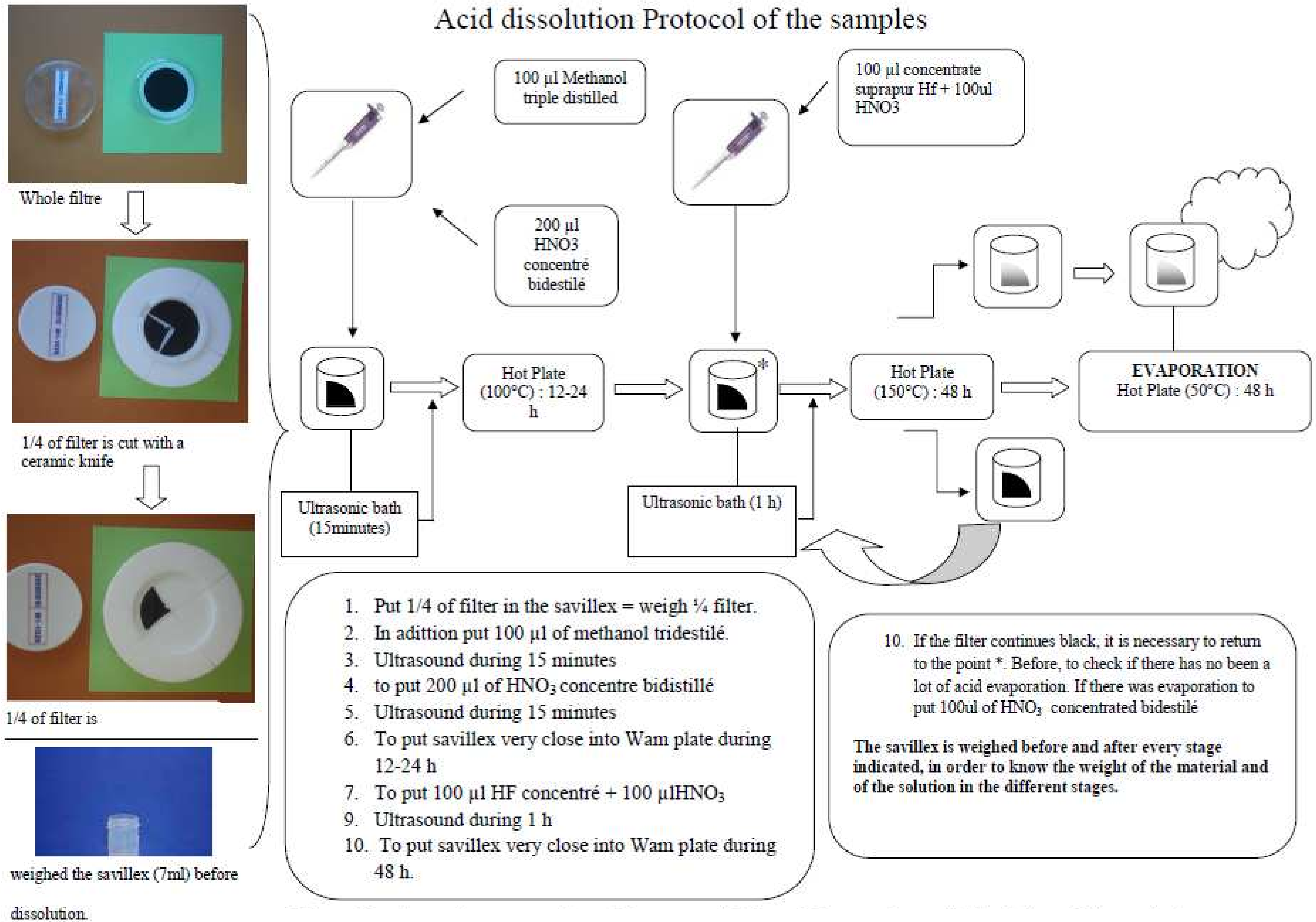
Major element and some trace element compositions of particulate matter published in Morata et al. (2008) were obtained with this technique. Detection limits, detailed experimental conditions and technical specifications are given in Morales et al. (1995) and Miranda et al. (2006). Data processing has been done by the technical and is also detailed in the articles mentioned here above.

2.5.3 ICP-MS analysis

They were performed on a Agilent 7500 equipped with a collision cell, at the LMTG.

2.5.3.1 Sample preparation

After cutting, each ¼ Teflon filter was weighted then put in a Savillex beaker (10ml) with 100µl of triple distilled Methanol (the required minimum volume to wet the hydrophobic filter) and 200µl of double distilled concentrated 14N HNO3. After a few tens of minutes in an ultrasonic bath, beakers were left for 12 to 24 hours at 100°C on a hot plate. After addition of 100µl suprapure 16N HF and 200µl concentrate 14N HNO3, beakers were left for 48 hours at 150°C. Generally at this stage, filters were white. They were removed with tweezers and rinced carefully with MilliQ water. The residual liquids were evaporated slowly at 50°C in order to avoid the loss of volatile elements. Nearly dry residues were recovered with 50µl concentrated HNO3, spiked with In-Re solution (internal standards) and diluted with MilliQ water for a HNO3 2.5%, 2ml final volume. The complete protocol together with some photos is given in figure 20. For quality control, a subset of samples was analyzed for the second time as duplicates. Total manipulation and chemistry blanks were associated with each series of sample.



1. Put 1/4 of filter in the savillex = weigh ¼ filter.
2. In adittion put 100 µl of methanol tridestilé.
3. Ultrasound during 15 minutes
4. to put 200 µl of HNO_3 concentre bidistillé
5. Ultrasound during 15 minutes
6. To put savillex very close into Wam plate during 12-24 h
7. To put 100 µl HF concentré + 100 µlHNO_3
9. Ultrasound during 1 h
10. To put savillex very close into Wam plate during 48 h.

10. If the filter continues black, it is necessary to return to the point *. Before, to check if there has no been a lot of acid evaporation. If there was evaporation to put 100ul of HNO_3 concentrated bidestilé

The savillex is weighed before and after every stage indicated, in order to know the weight of the material and of the solution in the different stages.

Figure 20: schematic representation of the protocol followed for complete acid dissolution of the particulate.

2.5.3.2 Data acquisition and processing

All trace elements were analyzed when possible on at least 2 isotopes and with two analytical modes: with or without gas in the collision cell. The element In was used as internal standard and Re as a control of the validity of the internal standardization. External calibration was done with (non matrix-matched) artificial solutions and the protocol applied for internal standard and interference correction followed the one described in Aries et al. (2000). Duplicates were run in order to control the whole analytical process: homogeneity of the grains spread on the filter, sample acid dissolution, ICP-MS reproducibility.

The raw data used by the ICP-MS software and validated by the technician had to go through a series of data processing before definitive data validation which include:

- When concentrations were measured independently with two isotopes of the same element, and two operating modes, selection was made of the best determination, taking into account the specific potential interference, the counting statistics and the error attached with each measurement.
- Elimination of the measured values that were lower than the detection limit
- Blank corrections

Initial concentrations measured as ppb in the 2ml solution were converted finally into µg/m^3 taking into the account the weight of the filter fraction, the total weight of the filter, and the air volume filtered for each sample (data from MACAM network). Duplicates were considered in order to appreciate our real accuracy and reproducibility.

Final selection of the measured elements: those which were either under the detection limits or suffered too high blank corrections for most samples were removed from the final table and not discussed in chapter 4.

2.6 Treatments processing of geochemical data

When facing results on hundreds of samples, for a few tens of elements, collected on 2 sites, for roughly 80 different days with different meteorological conditions, one has to use simplifying concepts and statistical methods in order to extract information that can be interpreted. These concepts and methods are presented below.

2.6.1 Enrichment factors (EF)

Enrichment factors (EF) help outline the influence of a contaminant source compared to a reference one. All measured elemental concentrations are normalized to a crustal element (typically Al, Zr or Th) chosen for its stability in most environmental processes. Then these normalized values are compared to their equivalent in a representative natural geological environment. The result: the EF, shows the level of enrichment of a given element compared to the natural geological environment. Here we used the mean bulk crust as defined by Taylor and Mc Lennan, (1995) as the reference natural geological environment.

EF are calculated as follows:

$EF_x = (C_x/C_{ref})_{\text{sample}} / (C_x/C_{ref})_{\text{crust}}$

where $(C_x/C_{ref})_{\text{sample}}$ is the ratio of concentration of an element x to the reference element in the sample and $(C_x/C_{ref})_{\text{crust}}$ is the same ratio in the typical crustal material. Here, we have chosen Al as the reference element. EF higher than 1 would show that part of the concerned element originates from other sources than crustal. But it is assumed generally that EF has to be above a threshold of 10 to be considered as a reliable proof of a non-crustal contribution to the budget of one element (Parehk et al., 1989).

2.6.2 Pearson Matrix (used in Morata et al., 2008)

The correlation measures the linear relation between two variables and their directions (direct or indirect). Therefore, the coefficient for a linear relation will be 1 or -1. When the value of the coefficient is zero or nearly zero, either there is no relation between the two variables, or the relation is not linear.

The Pearson correlation coefficient is obtained by calculating the covariance between the variables.

2.6.3 Factor Analysis (FA)

Principal Components Analysis (PCA) and Factor Analysis (FA) attempt to identify underlying variables, or **factors**, that explain the pattern of correlations within a set of observed variables (Reimann et al., 2008). Normally, it is used to reduce the original number of variables in order to identify a small number of factors that explain most of the variance, which can be observed in the much larger number of variables. The difference between PCA and FA is primarily that PCA accounts for maximum variance of all variables, while FA accounts for maximum inter correlations (Reimann et al., 2008).

In PCA, the reduction of dimensionality is achieved by transforming the group of original variables **p** into another group with a number **q** of uncorrelated variables **(q<p)** which names are Principal Components. If a large number of variables exist with high dependency between

them it is probable that a smaller number of new variables (< 20% of original variables) can explain the majority of the original variability (more than 80%) (Filzmoser et al., 2003). For n samples and p variables, the data set is a matrix = n x p (n > p), where the columns are the variables and the rows are the samples.

If the variables have the same importance it is better to use a correlation matrix, but if the variables have the same units and in addition one wants to emphasize each variable according to its variability, it is better to use covariance matrix. This criteria depends on the investigator.

2.6.4 Principal Component Analysis

The new variable q **(principal component)** has been obtained as a linear combination of the original variables. The components are organized as a function of percentage of variability. The direction in a variable space that best preserves the relative distances between the objects (samples) is a latent variable, which has **maximum variance** of the scores (these are the projected data values on the latent variable). Its direction is called by definition the first principal component (PC1).

PCA searches for the direction in the multivariable space that contains the maximum variability. In this way, the first component (PC1) will be most important because it explains the maximal variability of the data set. The second principal component (PC2) is orthogonal to PC1 and contains the maximum amount of the remaining data variability (Reimann et al., 2008).

All data points are orthogonally projected onto PC1, resulting in new data points, that are called scores of the first principal component. The score represents each data point with a single number along the new coordinate PC1. PC2 is in the direction orthogonal to PC1, again all data points are orthogonally projected onto PC2, resulting in the score PC2. The direction of each principal component is expressed by its loadings which convey the relation to the original variables.

PCA is a decomposition of the covariance, matrix or correlation matrix into “eigenvectors” and “eigenvalues”. The eigenvectors are the loadings of the principal components spanning the new PCA coordinate system. The amount of variability contained in each principal component is expressed by the eigenvalues, which are simply the variances of the score.

The PCA will be used as exploratory methodology in order to find the number of uncorrelated components that will be used as number of factors, which will be fixed in FA.

But, before using FA, it is necessary to verify that the data set has a normal distribution and the observations are independent. Indeed it is now well known amongst applied geochemists that regional geochemical data practically never show a normal distribution (Reimann et al., 2008). The presence of outliers values in the nature is very common In this case it is important that all the variables should come as close to normal distribution as possible (Reimann et al., 2008). In this case it is necessary to reduce the impact of outliers applying robust version of PCA or FA (Filzmoser, 1999; Pison et al., 2003). The aim is to fit the majority of data points, contrary to classical (least square) estimation where all data values, including the outliers are fitted. When using robust PCA or FA, the outliers can be identified and interpreted by studying the scores on the robust principal components factors.

PCA and FA require, in order to give stable data, that there are a sufficient number of samples compared to the number of variables. Different empirical rules have been suggested (Reimann et al., 2008), e.g., $n > p2 + 3p + 1$ (where n is the number of samples and p the number of variable (reference). Even if it exists rules adapted to each situation, for “small” data sets, PCA or FA should preferably not be used with the full set of elements.

CHAPITRE 3: MINERALOGIE

3.1 Introduction du chapitre

Santiago présente différents niveaux de pollution atmosphérique qui dépendent, entre autre: de facteurs météorologiques, de la position géographique à l'intérieur de la ville et des émissions de sources naturelles et anthropogéniques. La présence des Andes, à l'Est, et de la Cordillera de la Costa à l'ouest, dans un contexte bio-climatique de type méditerranéen caractérisé par une faible couverture végétale, suggèrent une contribution lithogénique importante dans le matériel particulaire. Néanmoins, est une mégapole qui génère d'importantes émissions d'origine anthropogénique qui se surajoutent aux émissions naturelles.

L'étude minéralogique a pour objectif de préciser la morphologie et la composition minéralogique des particules afin d'aider à la compréhension de leur provenance et de leur formation. Ces informations seront très utiles quand il s'agira de proposer des hypothèses sur les diverses provenances des éléments chimiques présents et sur les processus de génération.
A la différence de nombreuses études consacrées à la minéralogie des particules respirables, effectuées à Santiago ou ailleurs (Sandoval et al 1993, Morata et al., 2008), qui se focalisent souvent sur des grains remarquables, cette étude menée sur des filtres d'aérosols a été abordée d'un point de vue statistique, et basé sur une sélection aléatoire des particules de taille supérieure à 1µm distribuées sur une surface d'environ 400mm^2. Comme les filtres sont très chargés en matériel particule et en conséquence le nombre de particules analysées par échantillon varie entre 100 et 70 pour les PM 10 et pour les PM2,5.

A fin d'approfondir sur la provenance du matériel particulaire, nous avons travaillé sur deux sites en centre ville, présentant un fort impact anthropique (industries) (Teatinos et La Paz) et deux autres sites moins impactés en raison de leur localisation dans des quartiers plus résidentiels (Macul et Las Condes). De même, afin de caractériser et quantifier les différentes sources de pollution et leurs contributions respectives (en nombre de particules), nous avons sélectionné des échantillons prélevés à différentes saisons, et en particulier l'hiver, lors des épisodes de pollution.

Le présent chapitre comporte deux parties:

La première partie de ce chapitre est constituée par un article (Morata et al., 2008) présentant les premiers résultats obtenus sur les échantillons des stations Macul et Teatinos. Ce travail intègre différentes techniques analytiques (PIXE, DRX, mesures magnétiques) en couplage avec des observations détaillées au MEB, pour aider à la caractérisation de la phase solide des aérosols de Santiago du Chili et proposer des sources potentielles.

Durant ce travail, ma contribution a porté sur :

- l'acquisition des échantillons et mesures associées (mesures gravimétriques, T°, hygrométrie), conditionnement et stockage des échantillons, construction de la base de données regroupant ces informations ainsi que les informations météorologiques,
- l'acquisition des analyses par PIXE, sous la direction de Dina Torres (Université du Chili),
- l'interprétation minéralogique d'une partie des spectres multi élémentaires obtenus sur le MEB du LMTG (Toulouse), sous la supervision de M. Polvé,
- le classement et la construction d'histogrammes de présence de différentes phases minérales proposées.

La deuxième partie de ce chapitre est un complément de l'article précédent (Morata et al., 2005) , présentant une rapide interprétation des données chimiques obtenues au MEB sur quelques échantillons additionnels, dans les stations La Paz et Las Condes, sur lesquelles porte le travail de géochimie, ceci afin d'élargir et de compléter les données précédentes et d'aider à l 'interprétation des données géochimiques.

L'objectif central de cette partie est toujours la recherche de l'origine des particules analysées.

En conséquence, à partir de l'étude morphologique et de la composition chimique de ces particules, on propose quelques hypothèses concernant leur temps de résidence et leur dynamique physico-chimique. Ceci permet d'enrichir la discussion sur la formation des sels secondaires dans l'atmosphère et de préciser les sources potentielles émettrices de Fe, Ba, Zn, entre autres. Cette étude montre comment la caractérisation minéralogique peut aider à distinguer entre une origine liée aux activités d'extraction minière ou aux processus de fonderies.

Evidement un certaines nombre de problèmes analytiques limitent les possibilités de ce type d'étude, comme, par exemple, la taille et la position des particules incrustées dans la membrane du filtre d'analyse. Ceci joue un rôle dans la qualité des spectres, qui ne sont pas toujours représentatifs d'une phase minérale et qui peuvent parfois prêter à confusion, suite à la présence d'une pellicule recouvrant la particule à analyser. Néanmoins, l'étude donne aussi un certain nombre de spectres fiables permettant de discuter la nature des particules présentes dans l'air.

3.2 Résumé de l'article Morata et al., 2008

Le but de cette étude préliminaire appliquée à un petit nombre de filtres était de faire une caractérisation des différentes particules présentes dans l'air respirable de Santiago et d'obtenir une quantification de leurs proportions relatives. Deux sites différents, l'un, Teatinos, en centre ville et l'autre, Macul, dans le campus scientifique situé dans une zone résidentielle moins densément peuplée, ont été choisis. La comparaison des observations faites sur chacun des sites et entre les deux fractions granulométriques (PM10 et PM2.5) vise à permettre de montrer les similitudes et les différences dans les populations de particules observées et d'essayer d'en tirer des conclusions en termes de source.

Les analyses au MEB ont été effectuées sur 2 appareils différents, le premier à l'Université Catholique du Nord (Antofagasta, Nord Chili) et le deuxième au LMTG, Université de Toulouse. Les études statistiques au MEB portent sur un couple PM10-PM2.5 à Macul, completé par un autre filtre PM10 du même site et sur deux filtres PM10 de Teatinos.

Dans le même temps, des analyses PIXE ont été effectuées au laboratoire de Physique de l'Université du Chili sur 27 échantillons, 20 (10 PM10+10 PM2.5) provenant de Macul et 7 de Teatinos.

Les concentrations en éléments majeurs et métaux sont données dans l'article, ainsi que les histogrammes de répartition des différentes particules entre les différents sites et les 2 fractions.

Les observations générales sont les suivantes:

- Le total de ces concentrations, comparé à la masse d'aérosol sur le filtre, montre que les éléments mesurés contribuent pour environ 50 % du total à Macul mais seulement pour 10 % ou moins à Teatinos. Ceci montre que la majorité de la masse retenue sur les filtres de Teatinos n'est pas analysée, il s'agit très certainement du carbone élémentaire et de composés carbonés organiques, qui rendent les filtres de Teatinos complètement noirs (et conducteurs).
- Si on fait abstraction de la couverture de microparticules de C, on observe que, quelque soit la taille des particules (PM10 ou PM2.5) les particules d'origine lithogéniques sont les plus nombreuses (73% dans la fraction PM10). Cette observation à partir des données MEB (sur des particules > 1 µm) est confirmée par les données PIXE (sur l'ensemble des particules). Vient ensuite une catégorie de particules (oxydes de fer, sulfates de Ca et Ba, par exemple) sans forme significative et dont la formule chimique ne permet pas de trancher sur leur origine, lithogénique, atmosphérique ou anthropogénique. Enfin on observe des particules

d’origine clairement anthropogéniques (avec parfois des formes remarquables, telles des sphères) et de très rares particules d’origine biogénique.

- A Teatinos comme à Macul, ce sont les silicates (pyroxène, plagioclase, amphibole, argiles, quartz) et oxydes de fer qui dominent au sein des particules d’origine lithogénique. Viennent ensuite des sulfates et chlorures, les sulfates étant plus fréquents à Teatinos qu’à Macul. Enfin, les particules d’origine anthropogénique, et de composition parfois exotique, sont surtout présentes dans la fraction fine.
- Afin de quantifier la contribution de ces particules d’origine anthropogénique, des facteurs d’enrichissement ont été calculés, en utilisant Al comme élément de référence et en comparant à la composition chimique de la croûte continentale moyenne telle qu’estimée par Taylor et McLennan, (1995). Si on ne considère comme significatif que les facteurs d’enrichissement supérieurs à 10, on en déduit que Si, P, K, Ti, Ca et Fe ne sont apportés que par les particules lithogéniques, alors que S, Cl, Cr, Cu et Zn sont portés en majorité par des particules d’origine anthropogénique. Mais les facteurs d’enrichissement sont moindres à Macul qu’à Teatinos ce qui est en accord avec les observations faites au MEB.
- La pourcentage élevé de particules lithogéniques est typique des zones à climat méditerranéen semi aride à faible couvert végétal, où les particules de sol nu sont mobilisées par le vent. De plus, les particules observées au MEB sont typiques du cortège de minéraux présent dans les produits d’altération des roches volcaniques environnantes. Ces particules présentes aussi dans les parcs et les rues non goudronnées, sont constamment remobilisées par le trafic automobile et par l’habitude locale de balayage journalier des trottoirs et allées. Ces particules maintenues dans l’air à cause de la couche d’inversion très basse l’hiver, n’en sont retirées que lors d’épisodes pluvieux.
- Origine des oxydes de fer.

Les oxydes de fer existent dans les deux sites et les deux fractions granulométriques. Ces oxydes de fer peuvent être soit des magnétites provenant des roches magmatiques, soit des goethites secondaires développées dans les sols par altération des roches, soit enfin des particules anthropogéniques provenant de la dégradation des barreaux métalliques, des tubulures diverses utilisées dans l’industrie, des pots d’échappements etc. Aucune de ces particules ne présente de forme cristalline permettant de leur supposer une origine primaire magmatique. Au contraire elles se présentent sous forme de grains mal ou non cristallisés. Des études des propriétés magnétiques de filtres montrent que les oxydes de fer sont des magnétites, lesquelles ont aussi été observées sur des filtres, avec des aspects et des tailles compatibles avec nos observations. Nous supposons donc que la majorité des oxydes de fer présents sont d'origine anthropogénique (et provenant principalement des pots d'échappement), ce qui n'exclue pas la possible présence d'oxydes de fer provenant de l'altération des roches magmatiques.

- Origine des carbonates et sulfates de calcium.

Ces particules peuvent être d'origine soit lithogénique (intercalations sédimentaires), soit anthropogénique (carrières, cimenteries, carrières de gypse). Mais ces intercalations sédimentaires étant rares et les carrières et exploitations diverses de calcaire et de gypse beaucoup plus nombreuses aux alentours de Santiago, cette dernière origine est plus probable.

- Source de quelques particules d'origine anthropogénique.

Les éléments S, Cl, Cr, Mn, Cu et Zn présentent des facteurs d'enrichissement très importants, certainement dus à des processus d'origine anthropiques. De tels enrichissements avaient déjà été observés pour Cr, Mn, Cu et Zn et attribués à une grande variété de sources anthropogéniques : centrales thermiques, émission des véhicules, industrie de l'acier, combustion des ordures, hauts fourneaux etc. L'identification de sources précises ne peut se faire ici, avec les outils usuels de la géochimie. Néanmoins quelques pistes méritent d'être mentionnées. Par exemple S présente des EF importants dans les deux sites, et sans correlation avec Cu ou Zn, on peut dés lors écarter la possibilité que S provienne d'un sulfure naturel, il est plus probablement dans des phases sulfates, observés d'ailleurs au MEB. Ces phases proviendraient des 3 raffineries de cuivre situées à moins d'une centaine de km de Santiago.

Cl aussi est anormalement enrichi dans les aérosols de Santiago et il faut écarter l'hypothèse d'une origine marine car nous avons observé très peu de grains de NaCl au MEB, mais, en l'absence d'analyse des concentrations en Na il est difficile d'aller plus loin, tout en retenant une probable origine anthropogénique liées aux industries chimiques, à confirmer.

3.2.1 Conclusions

Cette étude préliminaire a montré que le couplage entre données géochimiques et obsevations minéralogiques se révèle, même s'il est imparfait, être un bon outil qui permet d'obtenir des informations originales sur l'aspect, la taille et l'origine des particules respirables et leur association avec certains éléments chimiques. Mis à part la contribution importante sinon majoritaire des particules de carbone, il est intéressant de noter que les particules d'origine lithologiques sont les secondes contributrices au bilan global. Le couplage entre observation, détermination minéralogique, propriétés magnétiques et teneurs en éléments majeurs permet de proposer des origines pour un certain nombre de particules d'origine discutable. Le calcul des facteurs d'enrichissement, en couplage avec les données géochimiques et la caractérisation minéralogique permet de suspecter l'origine de particules liées à des activités anthropiques typiques de Santiago. Mais sans données précises sur les concentrations en métaux toxiques, il n'est pas possible de faire le lien avec les problèmes épidémiologiques.

3.3 Article

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ORIGINAL ARTICLE

Characterisation of aerosol from Santiago, Chile: an integrated PIXE–SEM–EDX study

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Abstract Santiago de Chile is a big city with huge air quality problems, being one of the most polluted cities in the world. This is aggravated during winter by the topography and meteorological conditions of the city. Although public policies have been developed to minimise the atmospheric aerosol pollution, there is a lack of adequate knowledge and poor characterisation of these aerosols (in its $PM_{2.5}$ and PM_{10} fractions). In this study we sampled atmospheric particles during winter in two distinct areas of Santiago: downtown (Teatinos Street) and in a more residential area (Macul). Major (Si, Al, Fe, Ca and K) and some trace element (S, Cl, Ti, P, Cr, Cu and Zn) compositions were obtained by proton-induced X-ray emission (PIXE). Morphological, type and chemical characterisation was also performed using scanning electron microscopy (SEM) coupled with an energy dispersive X-ray microanalysis system (SEM–EDX). Besides the carbon particles, the contribution of which can be quite important in the atmospheric aerosol, especially in downtown, unambiguously lithogenic (i.e. of geological origin) particles and elements are the second highest contributors. Enrichment factor calculation, together with particle identification and element correlation allow the origin of some elements and particles to be traced, revealing anthropogenic origins for some of them that are specific to the Santiago area.

Keywords Atmospheric aerosol · Particle analysis ·←
Mineralogy · Geochemistry · Environmental pollution

Introduction

All mega and big cities in the world suffer from heavy atmospheric pollution, both from more or less toxical gases (NO, CO, O_3, etc.) and from very small solid particles inhaled by humans. This has become a major health issue and most megacities are now developing survey programs in order to identify these pollutants with the aim, of first, being able to forecast pollution peaks and ultimately, to attempt to reduce their amount. Recent research has shown a clear connection between high levels of atmospheric particles and adverse effects on human health (see references in Moreno et al. 2003, 2004b, Yadav and Rajamani 2004, among others). Therefore it becomes very important to characterise solid aerosols as best as possible, both mineralogically and chemically and to determine their sources.

The inhalable particulate matter suspended in the atmosphere is heterogeneous in size, composition and origin. Typically, any sample collected in a city with a

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problem of particulate matter pollution would contain different types of salts (mostly ammonium and calcium sulphates, ammonium nitrates, sodium chlorides) organic and elemental carbon (mainly derived from road traffic), biological components (pollen and micro-organisms), iron and other metal compounds derived from industrial processes, and minerals and rocks fragments derived from the surrounding geological formations. They can be defined as: organic and/or inorganic, natural (biological/geological) and/or anthropogenic, and primary and/or secondary. This diversity makes it difficult to identify pollutant sources as well as to model the particulate matter distribution in relation to meteorological parameters. Because of this diversity, estimation of the mass alone of the particle matter and its carbon content provides insufficient information about its origins and its potential health effects (Moreno et al. 2004a).

Typical geological analytical techniques for the identification of mineral phases and their chemical characterisation (e.g. scanning electron microscopy (SEM) coupled with microanalysis, X-ray diffraction and chemical analyses) have been recently applied in order to trace the origin of particulate matter in the atmosphere (e.g. Kasparian et al. 1998; Boix et al. 2001; Moreno et al. 2003, 2004a, b, c, 2005; Celis et al. 2004; Kruger et al. 2004; Yadav and Rajamani 2004; Suzuki 2006, etc) and provide valuable information both for scientists tracing the sources of these aerosols and for civil servants in charge of pollution reduction.

Santiago is one of the most polluted cities in the world, which is aggravated during winter by the topography and meteorological conditions of the city. Previous studies of particulate matter in the air of Santiago have been focussed on the application of optical techniques (e.g. Trier 1997; Gramsch et al. 2004; Koutrakis et al. 2005) or gravimetric methods for determination of the particle mass (Jorquera 2002) followed by the elaboration of statistical models to define its distribution and the establishment of atmospheric monitoring networks (Morel et al. 1999; Pérez and Reyes 2003; Silva and Quiroz 2003). However, no information has been available concerning the types of particles present in the air, and their origins. As previously shown by the other geologists (e.g. Moreno et al. 2004a, b, c, 2005), SEM, together with proton-induced X-ray emission (PIXE) are useful tools for the identification of the different particle types (e.g. Miranda and Andrade 2005; Cong et al. 2007) and the quantification of their relative proportions in particulate atmospheric matter. Here we applied these techniques to the particulate matter of Santiago, which allowed us to characterize and list all the different types of particles present, together with their variation between the two sites in relation to meteorological conditions. This preliminary study is part of a larger program, including chemical and isotopic analysis and magnetic characterization of the particles in a set of atmospheric samples collected in Santiago, Chile.

Geographical, meteorological and geological context

Santiago (33.5°S, 70.8°W), the capital of Chile, a city with almost 6,000.000 inhabitants (37.5% of the national population, http://www.ine.cl), is located on a gentle slope (from 450 m above sea level in the west to more than 750 m in the east) in a geographically confined basin (the Central Valley) between the Andean Cordillera (altitude >4,500 m) to the east and the coastal range (altitude up to 2,000 m), to the west (Fig. 1a, b). Due to its subtropical latitude, the vertical exchange of air during most of the year is controlled by permanent subsidence and the formation of a thermal inversion layer, caused by the South Pacific sub-tropical anticyclone. This results in a semiarid climate with temperatures ranging between −2 and 35°C (average values around 14°C) and an average rainfall of 350 mm per year but large interannual variability (Rutland and Garreaud 1995). The prevailing wind direction over the city is southwesterly throughout the year. The thermal inversion subsidence layer lies at about 400 m above the ground during winter and autumn and at 1,000 m during spring and summer. During these thermal inversion periods, the vertical ventilation is highly restricted and air pollution increases dramatically as a mass of cold air is trapped below warmer air. Consequently, the geography and climate of the Santiago basin are, in general, unfavourable for the diffusion of air pollutants. Extreme events of air pollution occur frequently during the high pollution season, extending from April to August (Rutland and Garreaud 1995). Moreover, the urban area is showing rapid growth, concentrating most of the new services, housing and industries as compared to the rest of the country (Romero et al. 1999), thus reinforcing the magnitude of this pollution problem.

Geologically, Santiago is located in a basin filled by quaternary alluvial sediments mostly derived from the chemical and mechanical erosion of the Cenozoic intermediate and basic volcano-sedimentary formations of the Andes (Fig. 1c). Three steep hills inside the city are composed of dacitic domes or necks covered by the same Quaternary alluvial material. The 450 ± 60 ka old Pudahuel rhyolitic tuff (e.g. Stern 2004) crops out along the western side of the town. Both the alluvium and rhyolitic tuff are unconsolidated and covered by scarce vegetation, which becomes dry in summer, leaving unprotected soils during a large part of the year.

Some active copper mines are present in the proximity of Santiago, including the world class El Teniente Mine.

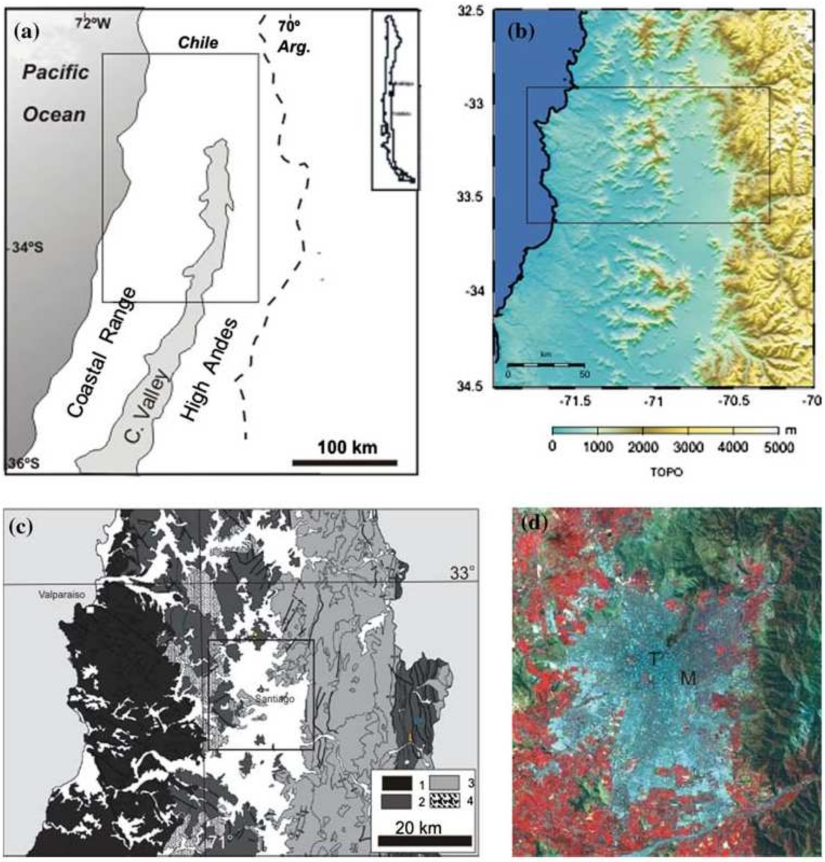


Fig. 1 Location, topography and geology of the Santiago de Chile area (based on the geological map of SERNAGEOMIN 2003) indicating the sampling sites. Symbols in **c**: *1*: pre-Mesozoic rocks, *2*: Mesozoic volcano-sedimentary rocks; *3*: Cenozoic volcano-sedimentary rocks; *4*: Cretaceous granitoids; Holocene-Quaternary in white. Legend in **d**: *T*: Teatinos Street; *M*: Macul site

Cu smelting industries are also located a few kilometres from the town.

Sampling and analytical techniques

Aerosol samples were collected at two different sites in Santiago (Fig. 1d), about 7 km apart: (1) downtown Teatinos Street, a canyon street used by many buses and lined by crowded sidewalks. Moreover, it is located 150 m from Alameda Street, a five-lane avenue (three of which are dedicated to buses), one of the most heavily used roads of Santiago; and (2) on the campus of the Faculty of Sciences at the University of Chile, located on the east side of the city in a residential area, 300 m away from two major roads.

Sampling in Teatinos Street (only PM_{10} fraction) was done using a stacked filter unit (SFU) sampler placed on the top of an eight-floor building (ca. 30 m above ground level). Samples were taken from 24 h, three times per week, for a total period of 12 weeks during the winter of 2004 (Table 1). One day classified as critical by the air quality national agency (ICAP value of 244, http://www.conama.cl, Table 1) was also sampled. On the campus (sampling referred to as "Macul"), the double PM_{10}–$PM_{2.5}$ collector was placed 2 m above ground level. Typical collection rates were around 18 L/min. Samples from Macul were collected during one week in June (10 samples), and those from Teatinos during 1 month in July–August 2004 (7 samples).

All filters, whatever their type (Teflon, quartz or polycarbonate), were gravimetrically analysed before and after sampling with a ±0.001 mg microbalance in order to determine the amount of collected particulate matter (Table 1). Sampling conditions and mass concentrations are shown in Table 1. The filters were stored under sterile Petri dishes and in constant humidity- and temperature-regulated chambers. Following an integrated procedure of characterization and identification of the particulate matter using destructive and non-destructive analytical techniques, each filter (47 mm diameter) was cut into four quarters with ceramic scissors in a clean room. One quarter

Table 1 Meteorological (internal data from the Department of Geophysics, University of Chile) and gravimetric (or $PM_{10-2.5}$ mass concentration) data

Sample	Sampling date	Timing sampling	$T_{max} - T_{min}$ (°C)	Relative humidity (%)	PM_{10} weight (mg)	$PM_{2.5}$ weight (mg)	ICAP
Macul							
1-1147	03/06/04	12:00–18:00	23.8 – 17.4	30.9	–	0.479	91
2-1148					0.232	–	
1-1149	04/06/04	5:00–11:00	13.4 – 8.1	61.2	–	0.114	127
2-1150					0.349	–	
1-1151	05/06/04	5:00–11:00	11.0 – 8.8	87.5	–	0.171	70
2-1152					0.130	–	
1-1153	06/06/04	5:00–11:00	10.2 – 4.0	83.0	–	0.153	55
2-1154					0.120	–	
1-1155	07/06/04	5:00–11:00	11.8 – 3.7	73.0	–	0.106	71
2-1156					0.106	–	
1-1157	08/06/04	5:00–11:00	12.5 – 9.6	61.7	–	0.153	77
2-1158					0.446	–	
1-1159	09/06/04	5:00–11:00	11.5 – 9.8	71.3	–	0.180	98
2-1160					0.239	–	
1-1161	10/06/04	5:00–11:00	6.7 – 1.3	86.7	–	0.114	45
2-1162					0.164	–	
1-1163	10/06/04	12:00–22:00	11.4 – 6.0	65.2	–	0.226	45
2-1164					0.440	–	
1-1165	11/06/04	13:00–17:00	15.6 – 11.5	32.0	–	0.117	70
2-1166					0.113	–	
Teatinos street							
S14F1	10/08/04	24 h	17.2 – 7.3	75.9	2.766	–	60
S12F1	05/08/04	24 h	14.1 – 3.5	70.6	1.604	–	38
S10F1	30/07/04	24 h	24.3 – 4.7	54.4	1.677	–	89
S8F1	28/07/04	24 h	13.3 – 5.6	77.9	1.892	–	11
S6F1	23/07/04	24 h	16.8 – 6.6	59.0	2.601	–	62
S4F1	20/07/04	24 h	14.0 – 9.6	68.5	0.717	–	74
S2F1	17/07/04	24 h	18.0 – 6.9	64.3	2.620	–	244

ICAP: particle air quality index (SEREMI-Salud Región Metropolitana, Chile)

was used for PIXE and then SEM analysis and the remainder was kept for other analytical measurements (magnetic characterization, chemical and isotopic analysis) currently in progress.

Mean major element (Si, Al, Fe, Ca and K) and some trace element (S, Cl, Ti, P, Cr, Cu and Zn) compositions of particulate matter were obtained by proton-induced X-ray emission (PIXE) using a 2.2 MeV protons flux produced by a KN3750 Van de Graaff electrostatic accelerator at the Physics Department of the University of Chile. Detection limits (0.03–0.3 mg/cm^2) and detailed experimental conditions and technical specifications are given in Morales et al. (1995) and Miranda et al. (2006). Data are reported in Table 2.

Characterization of the particles (morphology, type and chemistry) was performed using SEM coupled with an energy-dispersive X-ray microanalysis system (SEM–EDX). Some filters were examined at the Department of Geology of the Catholic University of the North (Antofagasta, Chile) with a JEOL JSM 5900 LV-SEM. Others were studied at the LMTG in Toulouse (France) with a JEOL JSM 6360 LV-SEM. As most filters, especially in Teatinos, were covered by very small aerosol carbon particles, they did not need to be coated for conductivity. However, we found, that a gold coating made the filters more resistant to the effects of the flux. As the SEM in Toulouse is adapted to environmental observation (biological samples) no filters studied in Toulouse required any preparation. In each studied sample, a square was randomly selected in which all particles exceeding 2 μ were analysed. Secondary electron images (SEI) were obtained together with their EDS spectra of the major chemical components

Table 2 PIXE elemental concentrations (μg/m^3) measured in aerosols from Santiago

Sample	Si	Al	Fe	Ca	K	Ti	Cr	Mn	Cu	Zn	P	S	Cl
Macul													
1-1147	1.471	0.219	0.809	0.420	0.151	–	–	–	–	–	–	0.555	0.054
2-1148	4.223	0.690	1.817	1.594	0.305	0.108	–	–	–	0.125	–	0.389	0.113
1-1149	1.641	0.360	0.307	0.118	0.148	–	–	–	–	–	0.022	0.573	
2-1150	7.242	1.352	–	1.413	0.328	–	–	1.358	–	–	0.071	0.683	
1-1151	1.168	–	0.802	0.193	0.417	–	–	–	–	–	–	1.754	
2-1152	6.574	1.279	0.994	1.184	0.197	–	–	–	–	–	0.071	0.856	–
1-1153	0.423	–	0.359	0.134	0.170	–	–	–	–	–	–	0.725	–
2-1154	3.601	0.803	0.525	0.416	0.136	–	–	–	–	–	0.031	0.403	–
1-1155	1.031	–	0.526	0.290	0.229	–	–	–	–	–	–	0.591	–
2-1156	4.824	0.794	0.965	0.801	0.188	–	–	–	–	–	0.036	0.360	–
1-1157	1.282	0.200	0.637	0.295	0.326	–	–	–	–	0.139	–	0.562	–
2-1158	11.126	2.027	3.876	2.355	0.750	0.090	0.158	0.235	–	–	0.049	1.362	0.149
1-1159	0.496	–	0.384	0.189	0.258	–	–	–	–	0.205	–	0.550	–
2-1160	8.298	1.674	1.892	1.373	0.422	–	–	–	–	–	0.095	0.915	–
1-1161	0.811	–	0.467	0.225	0.146	–	–	–	–	–	–	0.258	–
2-1162	8.773	1.529	1.784	1.383	0.294	0.118	–	–	–	–	0.038	0.520	0.098
1-1163	0.881	–	0.601	0.280	0.172	–	–	–	–	0.132	–	0.416	0.050
2-1164	6.727	0.961	2.828	2.140	0.413	0.127	–	0.089	–	–	–	0.424	0.155
1-1165	1.685	–	1.081	0.537	0.216	–	–	–	–	–	–	0.675	–
2-1166	5.431	0.914	2.439	1.760	0.343	0.138	–	–	–	–	–	0.393	0.107
Teatinos street													
S14F1	18.232	7.379	20.547	14.911	7.733	1.894	1.370	0.888	0.925	1.502	–	9.116	3.551
S12F1	25.547	10.426	27.251	19.479	9.069	2.048	1.348	1.198	0.760	1.901	–	8.127	4.192
S10F1	4.133	1.384	5.420	3.669	1.662	0.369	0.303	0.197	0.094	0.200	–	0.967	0.441
S8F1	2.326	0.902	2.340	1.618	0.834	0.193	0.199	0.100	0.071	0.197	–	0.753	0.494
S6F1	1.441	0.504	1.541	1.007	0.599	0.104	0.106	0.069	0.067	0.072	–	0.546	0.787
S4F1	1.129	0.651	1.186	0.887	0.408	0.087	0.076	0.051	–	0.101	–	0.282	0.418
S2F1	2.067	1.234	2.264	1.288	0.996	0.130	0.090	0.072	0.120	0.229	–	0.622	0.483

(–) Below detection limit

present in each individual grain. This information allowed, in most cases, the identification of the grain and its origin (geological, biogenic, anthropogenic or atmospheric).

Statistical data were obtained on two types of filter: polycarbonate and Teflon. Both contain chemical components that could interfere and bias the interpretation. Therefore clean filters were first analysed in order to obtain their chemical spectrum. Polycarbonate filters have a very smooth surface in which particles appear clearly, whereas on the Teflon filters the fibrous surface can sometimes cause confusion between very small particles and Teflon glomerules on the lattice. Moreover, Teflon filters always provide C and F peaks that can disturb the EDS spectrum of very small grains ($\approx 1\ \mu$) whereas polycarbonate filters only contribute to the C peak.

With the optical resolution of both SEM, particles smaller than 1 μ could not be analysed correctly. Unfortunately, in many cases important geological information was thus lost, so that all the observations and conclusions are valid only for particles larger than 1 μ. Further work with HR-TEM will be needed to get information on these smaller particles. This is of crucial importance because, as we will see later, it seems that the type and origin of the particles vary in relation to their size.

Here we present a preliminary classification of the particle types we found, based on more than 300 grain identifications collected in five samples—three from downtown (Teatinos) and two from the campus (Macul).

Results

Gravimetric data

Particulate matter daily weights range from 0.1 to 0.45 mg in Macul where sampling lasted an average of 6 h, and from 0.7 to 2.8 mg in Teatinos, where it lasted 24 h (Table 1). In Macul, where two sizes were sampled, the PM_{10} weights were heavier than those of the $PM_{2.5}$, with the 03/06/04 sample being the exception. If calculated back to the same sampling time (24 h), recalculated sample weights in Macul vary from 0.424 mg (07/06/04) to 1.784 mg (08/06/04). In Teatinos they vary from 0.717 mg (20/07/04) up to 2.766 mg (10/08/04). Clearly, the particulate matter content is higher in Teatinos than in Macul. Due to the small number of samples studied, however, we did not detect statistically significant relations between sample weight and atmospheric and meteorological conditions.

PIXE data

PIXE analyses were performed on 27 samples, 20 from Macul (10 for the PM_{10} and 10 for the $PM_{2.5}$ fractions) and 7 from Teatinos. Elemental concentrations (expressed as $\mu g/m^3$) are given in Table 2. We expressed the data in $\mu g/m^3$ because this is the unit traditionally used in atmospheric chemistry and because it is representative of what is inhaled by the inhabitants, even if this concentration unit is geologically non-significant. We consider the filter deposit to be homogeneous and the data to be representative of the whole filter concentration. The total of these concentrations compared to the sample mass showed that the measured elements contribute up to roughly 50% of the sample mass in Macul but less than 10% of the sample mass in Teatinos. This means that most of the constituents in Teatinos were not analysed; they are probably elemental carbon and organic carbon compounds, as indicated by the black colour of the filters.

In general, of the 13 analysed elements, Si, Al, Fe and Ca (typical lithogenic elements) dominate. Si (Al), P, S and Cl are present as anionic groups (silicate or Al–silicate, phosphate, sulphide and/or sulphate and chloride, respectively), whereas Fe, (Al), Ca, K, Ti, Cr, Mn, Cu and Zn are mostly present as cations in combination with the former anion groups.

Element concentrations in filters from Teatinos were always one order of magnitude higher than those from Macul. This could simply reflect the heavier weight of the Teatinos samples when compared to Macul due to the longer sampling time together with higher particle concentration in the air in Teatinos. At the same time, the measured element fraction from Teatinos is a small part of the total matter. Thus no sound conclusions can be drawn from these raw concentrations in $\mu g/m^3$. As a consequence, correlation matrix coefficients have been calculated (Table 3) with the aim of understanding the chemical composition of the particulate matter. Diagrams based on elements ratios have also been used as they allow sources with different element ratios to be identified.

In the Macul samples, some important differences were observed between the two size fractions analysed. In the $PM_{2.5}$ significant positive correlations were observed only between Ca and Fe (Table 3a). Nevertheless, if elements with only three analyses are considered in the statistics (samples in italic in Table 3a), a positive correlation ($r > 0.8$) was found between Si and Al, as well as Al and S, and a negative correlation between Al and Ca, Al and Fe, Si and Zn, Ca and Zn, and Fe and Zn. A positive correlation between Si and Al would be indicative of the presence of Al–silicates, whereas a negative Fe–Zn correlation could indicate the presence of Fe-oxide minerals. The positive Ca–Fe correlation suggests ferromagnesian silicates, where Ca is always present (pyroxene and/or amphiboles).

In the PM_{10} fractions of the Macul samples, positive correlation was found between Si–Al, Si–S, Al–S, Si–K, Cl–Ca, Cl–Fe, Ca–K, K–Fe and Ca–Fe, and a negative correlation between S and Ti (Table 3b). Moreover, if samples with only three data (values in italic in Table 3b) are also considered, a negative Ca–Mn correlation is also observed. The fact that a better correlation exits in the PM_{10} fraction than in the $PM_{2.5}$ fraction could be due to either: (1) higher absolute element concentrations in PM_{10}, which allow higher measurements and, consequently, improve the r factor; and (2) a higher quantity of discrete minerals controlling the whole chemistry. Indeed, silicate minerals are presumed to be present in this fraction as evidenced by the high Al–Si-element ratios.

In the Teatinos samples, from which samples S14F1 and S12F1 were excluded due to their very high elemental concentrations, a very good correlation coefficient was found between almost all elements except Cl, Cu and Zn (Table 3c). This might indicate a better-defined mineralogy for the particulate matter but could also reflect the higher quality of the measurements due to higher concentrations. The chemistry of these samples could be explained by the presence of both felsic and mafic Al–silicates (as evidenced by the good Al–Si and Si–lithophile and transitional element correlations). Sulphate, and/or sulphide minerals are probably present too, as evidenced by the good correlation between S-K/Ca and S-transitional elements (Fe, Mn, Cr, Ti).

The diagram Si/S versus Si/Al (Fig. 2a) shows that the Si/Al ratios in Macul samples (whatever the size fraction considered) are always greater than those from Teatinos. This implies the occurrence of a higher amount of polymerized silicates in Macul (probably tectosilicates) with respect to Teatinos (which might have higher amounts of inosilicates and/or phyllosilicates). Moreover, the Si/S ratio in the PM_{10} fraction from Macul is 12 times the value found in the $PM_{2.5}$ from Macul or the Teatinos

Table 3 Correlation matrix (Pearson's coefficient) of elements measured by PIXE in the particulate matter from Santiago

(a) Macul Fraccion F1 ($PM_{2.5}$)

	Al	Si	S	Cl	K	Ca	Fe	Zn
Al	1.000							
Si	*0.902*	1.000						
S	*0.854*	0.110	1.000					
Cl		–	–	1.000				
K	−0.602	0.022	0.776	–	1.000			
Ca	*−0.862*	0.540	−0.149	–	−0.058	1.000		
Fe		0.575	0.333	–	0.314	0.864	1.000	
Zn	*−0.900*	*−0.810*	0.515		0.160	*−0.975*	*−0.975*	1.000

(b) Macul Fraccion F2 (PM_{10})

	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe
Al	1.000									
Si	0.958	1.000								
P	0.442	0.321	1.000							
S	0.896	0.822	0.461	1.000						
Cl	0.267	0.371	–	0.490	1.000					
K	0.714	0.800	0.231	0.738	0.703	1.000				
Ca	0.440	0.624	0.301	0.439	0.926	0.851	1.000			
Ti	−0.645	−0.595	–	−0.808	−0.341	−0.701	−0.377	1.000		
Mn	−0.047	−0.306	–	−0.147	–	*−0.572*	*−0.948*	–	1.000	
Fe	0.544	0.700	0.156	0.526	0.800	0.943	0.956	−0.473	–	1.000

(c) Teatinos (without the two first samples with very high concentrations)

	Al	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn
Al	1.000											
Si	0.831	1.000										
S	0.739	0.930	1.000									
Cl	−0.587	−0.348	−0.108	1.000								
K	0.893	0.978	0.911	−0.318	1.000							
Ca	0.760	0.983	0.864	−0.351	0.945	1.000						
Ti	0.751	0.987	0.898	−0.352	0.936	0.993	1.000					
Cr	0.624	0.940	0.900	−0.270	0.853	0.945	0.974	1.000				
Mn	0.717	0.981	0.891	−0.283	0.933	0.995	0.996	0.968	1.000			
Fe	0.811	0.991	0.884	−0.338	0.975	0.994	0.984	0.921	0.986	1.000		
Cu	0.768	0.256	0.113	−0.591	0.457	0.171	0.113	−0.118	0.081	0.266	1.000	
Zn	0.895	0.627	0.650	−0.585	0.680	0.497	0.530	0.456	0.469	0.555	0.721	1.000

(a) Macul samples, $PM_{2.5}$ fraction. (b) Macul samples, PM_{10} fraction. (c) Teatinos samples, excluding S14F1 and S12F1. In all cases, only variables with $n > 3$ have been considered. Variables with $n = 3$ are in italic

PM_{10} samples. The very high S content in the latter two samples could be related to a high sulphide, sulphate or sulphur content. Indeed, a highly positive correlation value ($r = 0.884$) between S and Fe in the Teatinos samples indicates the occurrence of pyrite (or any other Fe-bearing sulphide). High correlation values between S and K ($r = 0.776$ in the Macul $PM_{2.5}$ fraction; $r = 0.738$ in the Macul PM_{10} fraction and 0.911 in Teatinos PM_{10} fraction) could be related to potassium sulphate, the origin of which will be discussed later. The PM_{10} fractions of Macul display high S/Cl ratios (from 3 to 6), as compared to those of the Teatinos PM_{10} fraction (<2.5, Fig. 2b). This could be explained by the relatively low chlorine content in the first fractions. Nevertheless, the high Cl content in the Teatinos samples, associated with the lack of correlation between Cl and any other analysed element

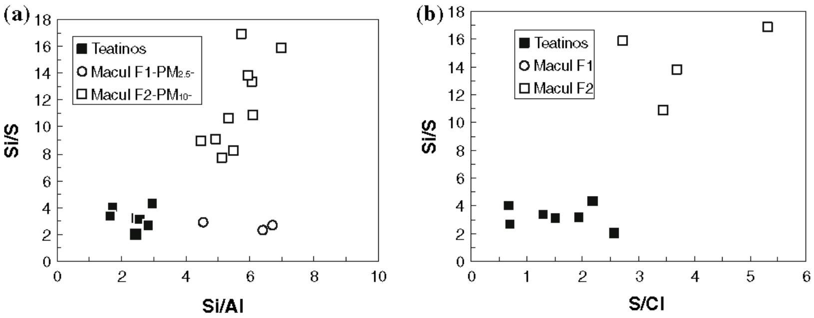


Fig. 2 Binary plots of element ratio measured by PIXE from aerosol particulate matter in Santiago, Chile. **a** Si/Al vs Si/S ratios; **b** S/Cl vs. Si/S ratios

(Table 3), probably reflects its association with non-analysed elements (most probably Na).

SEM data

This preliminary result is based on statistical data obtained from a couple of $PM_{10}/PM_{2.5}$ filters from Macul, complemented with data from another PM_{10} filter (samples 2-1150). For Teatinos Street, statistical data were obtained from two PM_{10} filters (S4F1 and S8F1), complemented with observations on a third (S7F1, not listed in Table 1). Meteorological conditions during sampling are summarised in Table 1.

Even before any microscopic work, it is evident that all filters from Teatinos (downtown area) are black, all covered with elemental (EC) or organic (OC) carbon nanoparticles, whereas filters from Macul (a more residential area) are beige. Moreover, in Teatinos, OC/EC ratios have been measured on eight size fractions of two samples (Leiva et al. 2005). Within each sample, variations of the OC/EC are bimodal, with one peak at the 0.18 μm fraction and the other peak between the 3.2 and 18 μm fractions. The 0.18 μm OC/EC peaks of the two samples reach 6.9 and 8.2, respectively, and those of the 3–18 μm fractions have values of 5.5 and 2.5, respectively. These figures are interpreted as typical of a secondary origin for these very small (0.1–1 μm) carbon compounds (Castro et al. 1999), which could originate from the intensive traffic. To summarize, Teatinos samples are loaded with more particles (for the same sampling time) than Macul samples, among which many complex carbon particles from exhaust pipes.

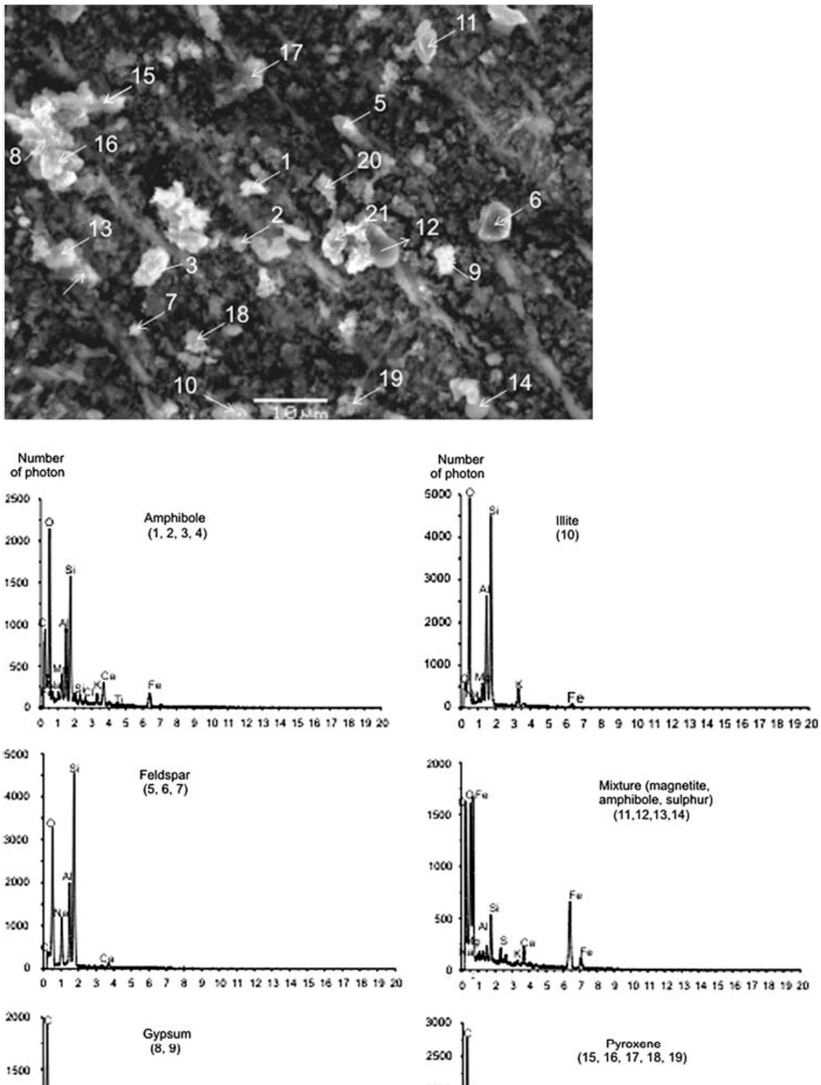
Most grains have irregular shapes where it is difficult to recognize any mineral feature. They sometimes form aggregates and very seldom show specific shapes, generally spheres, but also ovaloids, smooth tiles, etc. (Fig. 3). Grain abundance is higher in the Teatinos filters than in Macul, where the free filter surface can be observed between grains.

SEM interpretations are mostly based on the EDS chemical spectrum of the particles, which allows the different Al silicates, the ferro-magnesian minerals, and other inorganic and organic phases to be characterised. However, these spectra are disturbed by the fact that these minerals do not expose their flat surfaces to the RX gun, as they are grains randomly scattered on the filters. Therefore relative peak heights are meaningless, sometimes leading to ambiguous determinations noted as “non-characterised Al silicates”, for example. Beside its chemical spectrum, the shape of the particle is always considered as being very regular, spherical for example, and even if associated with a typical Fe oxide or an Al oxide formula, it would not be interpreted as a geological feature. Moreover, $CaSO_4$, which corresponds to both natural gypsum and industrial plaster, would be interpreted to reflect the regional geology, but also of the occurrence of quarries or building construction. Finally, there are cases where the ambiguity in the interpretation cannot be solved; for example it is difficult to decide if the many Fe oxides are natural or anthropogenic, when corresponding grains have no specific shape. All in all, errors in the interpretation might exist, but this changes none of our general observations and conclusions.

1. Nature of the particles and their distribution in both sites: site effect.

The most striking observation is that, beside the C cover, whatever the filter size and the site considered, geological particles are the most numerous. Indeed, Fig. 4 shows that on the two PM_{10} filters from Macul (sample 2-1164) and Teatinos (sample S8F1) unambiguous minerals such as plagioclase, pyroxene, phyllosilicates, clays and quartz contribute 66–73% of the total of the identified particles. Other inorganic compounds (Fe oxides, Ca and Ba sulphates) corresponding to grains devoid of typical forms

Fig. 3 SEM image of particulate matter with characteristic EDX spectra. Particles 20 and 21 correspond to titanite and barite, respectively (EDX spectra not shown)



and which could be either of geological or atmospheric/anthropogenic origin will be discussed later. Finally, presumably anthropogenic grains with striking features (spheres) and various compositions and biogenic remains account for the rest of the particles.

(a) Geological particles

In the two PM_{10} samples from the two sites, the frequency of minerals decreases in the order pyroxene, plagioclase, amphibole, clay, silica, and iron oxides. Some discrepancies

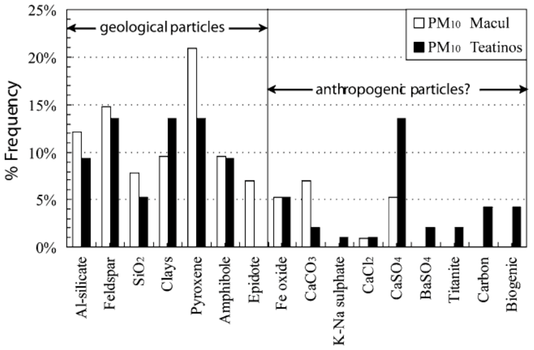


Fig. 4 Histogram frequency of air particles identified by SEM–EDX on PM_{10} filters from Macul (sample 2-1164, 115 analysed particles) and Teatinos (sample S8F1, 97 analysed particles)

also occur between the sites. Epidote-group minerals exist in Macul but not in Teatinos. $CaCO_3$ occurs with a greater percentage in Macul than in Teatinos, while $CaSO_4$ shows an inverse pattern. $CaCO_3$ and $CaSO_4$ spectra could correspond to limestone and gypsum, respectively, but their presence and concentration could also be related to human activity ($CaCO_3$ quarries and plaster used in construction). This also applies to iron oxides which are observed here but could be either natural, from surrounding soils, or anthropogenic. Only iron oxides, which appear as spheres are clearly anthropogenic.

Pyroxenes and amphiboles generally display EDX spectra (Fig. 3) showing no clear difference in composition between the two sites. In Macul, 10 of 15 plagioclase grains are albites, the rest being intermediate plagioclases, and only 1 K-feldspar was identified. In Teatinos, half of the grains are albites and half intermediate plagioclases. All grains have weathered irregular surfaces and shapes, which could suggest a secondary origin. Clays at both sites are generally illites, but some grains have spectra closer to that of montmorillonite.

(b) Other particles

Other particles include sulphates (KSO_4, $NaSO_4$, $BaSO_4$), chlorides ($CaCl_2$), exotic particles such as titanite (two grains), carbon (EC or OC) grains with specific shapes (spheres, tiles) and biogenic remains. They are nearly inexistent in Macul but reach 14.6% of the total in Teatinos. Sulphates have either an anthropogenic or atmospheric origin, while carbon is clearly anthropogenic. In addition to the C spheres, we also found spheres of Fe oxide, alumina, Cu alloy and Ti oxide. All exist as unique grains, but confirm the great heterogeneity of these anthropogenic particles. The combination of their low frequency and diversity will make the identification of each source difficult, but is worth noting.

Biogenic grains have been found in very small quantities and only in Teatinos. They are not pollen, but insect more probably remains. This agrees with the fact that our sampling was done in winter when biogenic activity is at a minimum.

2. The nature and distribution of the particles between PM_{10} and $PM_{2.5}$ fractions (Macul): size effect

A comparison between the nature of grains nature and their frequency in the two fractions of a sample collected in Macul is given in Fig. 5.

The nature and percentage of clearly geological particles are different in the two fractions. Micas are not present in the PM_{10} fraction while epidote-group minerals are absent from the $PM_{2.5}$ fraction. Pyroxenes and amphiboles are notably less numerous in the $PM_{2.5}$ fraction than in that of the PM_{10}. This can be attributed to the mechanical resistance of these minerals, which therefore survive as larger grains throughout all transport processes, as opposed to plagioclase and feldspar, which break more easily and occur in roughly the same proportions in both fractions. Silica behaves similar to plagioclase, which is an argument for assuming that they are not quartz grains which have a

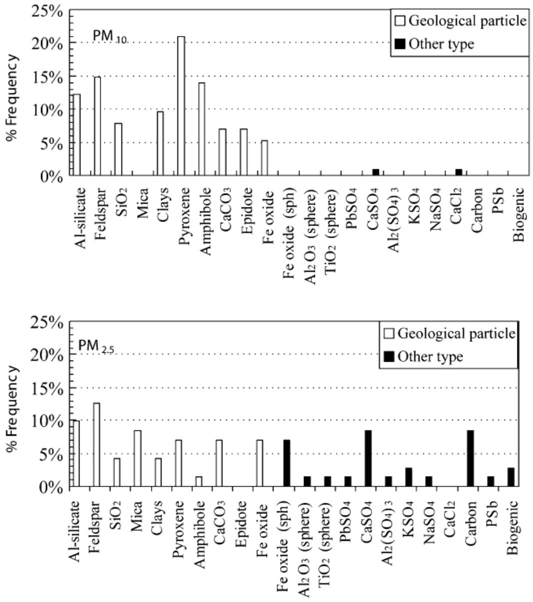


Fig. 5 Histogram frequency of air particles identified by SEM–EDX on PM_{10} and $PM_{2.5}$ filters collected from Macul (sample 2-1164, 115 PM_{10} analysed particles, SAMPLE 1163, 71 $PM_{2.5}$ analysed particles)

high mechanical resistance but more probably amorphous silica. $CaCO_3$ also exists in the same proportions in the two fractions, for the same reason or because of the same anthropogenic influence on both fractions.

Strong differences exist in the respective proportions of the non-geological particles between PM_{10} and $PM_{2.5}$. The latter has a higher global content in these particles together with a greater diversity in their composition. This might have strong implications for the health impact of $PM_{2.5}$ as compared to PM_{10} because both the sulphates, sulphides and metal compounds can release chemicals more easily than silicates.

3. The nature and distribution of the particles in relation to the date (meteorological conditions)

Statistical data on two PM_{10} filters from Teatinos, taken at an interval of 1 week during the most polluted season are plotted in Fig. 6. The most important feature concerns the non-geological particles, where sample S4F1 contains spheres of various compositions and NaCl grains of atmospheric origin, while S8F1 contains more $CaSO_4$ grains. Sample S4F1 also contains more Fe oxides, less pyroxene and amphiboles and no clay compared to sample S8F1.

Discussion

The PIXE and SEM analyses give convergent information concerning both the general mineralogy of the particles and their origins. Thus is important as the PIXE gives information derived from all particle sizes in samples while the SEM deals only with particles greater than 1–2 µm. Both techniques confirm that besides C-bearing nanoparticles, lithogenic minerals constitute an important to major part of all particles.

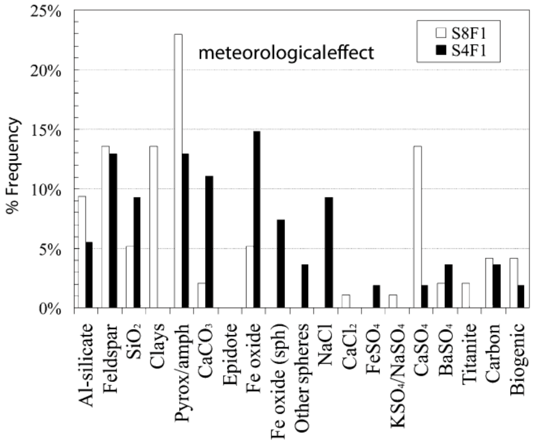


Fig. 6 Histogram frequency of air particles identified by SEM–EDX on PM_{10} filters collected at the same site (Teatinos Street) during two different sampling days. Sample S8F1, 96 PM_{10} analysed particles; sample S4F1, 54 PM_{10} analysed particles)

Both the PIXE and SEM confirm that felsic Al–silicates dominate in the Teatinos samples and are also present in the Macul samples, associated with a more complex mineralogy. Sulphates and chlorines are also present at both sites, with a higher content in S-bearing components in Teatinos with respect to Macul as shown by both the S content and SEM observations. Highly positive correlations between S-transitional elements and S-lithophile in Teatinos samples can be explained by a higher sulphide and sulphate content.

The combined SEM–EDX study allows the identification of both lithogenic and anthropogenic particles and their potential origin, but it does not give many clues concerning the origin of the chemicals. This problem also arises when studying soils and potentially polluted water. Calculating enrichments factors (EF) is a powerful tool commonly used for tracing the anthropogenic contribution in chemical budgets. Following the methodology described in Cong et al. (2007), the EF of elements in aerosols relative to the upper crust composition is defined by the expression:

$$EF_X = \frac{(C_X/C_R)_{aerosol}}{(C_X/C_R)_{crust}}$$

where X represents the element to be considered, EF_X is the enrichment factor of X, C_X the concentration of X, and C_R the concentration of a reference element. According to this expression, elements with EF values close to unity would indicate a strong crustal origin, while high EF values could indicate a non-crustal (including anthropogenic) origin. In our study, because Al is abundant in crustal materials and is not involved in anthropogenic particles, it was used as the reference element and, consequently, EF_{Al} will be 1.

Because the chemical composition of the different lithologies present in the geological environment of Santiago does not necessarily have the same chemical composition as the average Upper Continental Crust as estimated by Taylor and McLennan (1995) and used for the EF calculations, only elements with EF higher than ten could be considered to have a high non-crustal (anthropogenic?) origin. Calculations of EF are represented in Fig. 7, in which Si, P, K, Ti, Ca and Fe present EF values <10, suggesting an origin dominated by geological sources (soil and dust). On the contrary, S, Cl, Cr, Cu and Zn (and to a lesser extent Mn) display EF >> 10 and, consequently, a variable and high contribution (100–1,000 times) of non-crustal (anthropogenic?) origin would be proposed. It is

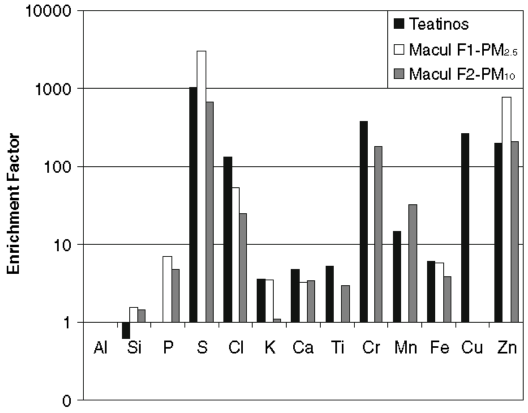


Fig. 7 Average enrichment factors of elements (PIXE determinations) derived from the average Upper Continental Crust (Taylor and McLennan 1995; S and Cl data from Rudnick and Gao, 2003) of the aerosol particulate matter in Santiago, with Al as the reference element

worth noting that the difference in EF in the Macul site for Zn and S between the $PM_{2.5}$ and PM_{10} fraction, being higher in the first one, indicates an element partition based on the particle size and origin, thus confirming the SEM observations.

Sources of the particles

The air particles in Santiago are a mixture of lithologic, biogenic and anthropogenic particles with proportions varying with the location, the date and the particle size. If lithogenic particles are clearly primary, some salts can have a secondary origin, being synthesized in the atmosphere from chemicals whose origin is generally related to human activity. The relative contribution of each source could be a function of dominant winds and location compared to major pollution centres. Based on our PIXE + SEM–EDX study, we have identified the particle nature and estimated their relative percentages in the two sampling sites. Some hypotheses can be proposed with respect to the source of these different particles. Moreover, specific chemicals have been found, through their high EF, to be enriched in the particles mainly due to anthropogenic activity.

Sources for the geological particles

The high percentage of geological particles in the air is typical of semi-arid climates where soils and rocks are not protected by a dense vegetation cover and can be transported by the wind (e.g. Yadav and Rajamani 2004). In fact, most of the geological particles identified on the filters are typical of the surrounding volcanic rocks (pyroxene, amphibole, plagioclase, feldspar) or their alteration/weathering products (clay minerals, epidote-group minerals, etc.). Parameters such as mineral resistance and density would control the relative proportion of these minerals at the different sampling sites. The high erosion rate of the mountains around Santiago is favoured by the low vegetation cover. These fine materials are also present on the streets, the parks and sidewalks. They are permanently remobilised by the intense traffic and, consequently, the finer particles stay suspended in the air during low wind circulation and fair weather conditions. Moreover, intense daily sweeping of all dirt footpaths and alleys together with the existence of dirt streets within the greater city exacerbate the problem. During winter, the inversion layer is at a fairly low altitude over the city and acts as a lid, keeping all these constantly remobilised particles in the air as long as it does not rain. Only rain events will clean the air of all these lithogenic particles.

Origin of Fe oxides

Fe oxides are ubiquitous, existing at both sites and in both size fractions. Fe oxides could be primary magnetites from the magmatic rocks, secondary goethite in the soils formed during weathering of the rocks, or they could be anthropogenic particles from the weathering of all Fe bars, tiles, exhaust grating equipments or from vehicles, exhaust pipes. None of the observed Fe oxide particles have crystal shapes compatible with them being primary lithogenic magnetite. On the contrary, they appear to be poorly to non-crystallised, shapeless grains. The magnetic properties of the same filters support the hypothesis of Fe oxides being magnetites (Silva-Padilla 2005). Moreover, Matzka and Maher (1999) and Muxworthy et al. (2001) also demonstrated the occurrence of magnetite in air particles, their sizes ranging between 0.3 and 5 µm, whose assumed origin was from vehicles exhaust pipes. Their observed sizes are compatible with the present observations. Therefore most observed Fe oxides are assumed to be poorly crystallised magnetites with an anthropogenic (traffic-related) origin. However, we cannot exclude the presence of some lithogenic alteration-related Fe-bearing minerals.

Origin of $CaCO_3$ and $CaSO_4$ particles

$CaCO_3$ and $CaSO_4$ particles could have both lithogenic and anthropogenic sources. Due the geological nature of the studied area, which is dominated by basic to intermediate volcanic and/or volcaniclastic rocks with very few sedimentary intercalations (which could be natural sources for these particles), it is assumed that they are disseminated in the same way as the silicates. However, cement industries exist a few kilometres north of Santiago in the proximity of a limestone quarry. As for $CaSO_4$, small gypsum quarries are exploited in the Cordillera roughly 70 km northeast of Santiago. Thus $CaCO_3$ and $CaSO_4$ particles could have a lithogenic origin, with their contribution to the general budget being amplified by human activity. Another probable origin for $CaSO_4$ could be related to the neo-formation of salts in the atmosphere as a result of reactions between sulphate (and carbonate?) anions, themselves formed by atmospheric SO_2 oxidation (Morales and Leiva 2006), and Ca^{2+} (Ba^+) cations.

Sources of the different anthropogenic particles

High to extremely high EF values have been found for S, Cl, Cr, Mn, Cu and Zn as shown in Fig. 7. Thus the potential anthropogenic control on their origin and recycling should be checked. Previous studies have shown that Cr, Mn, Cu and Zn could be anomalously enriched in aerosol particulate matter from a variety of anthropogenic sources: emission from fossil fuel combustion, motor vehicle emission, traffic-related sources, the steel industry, solid waste dumping, industrial metallurgical processes and waste incineration (Isakson et al. 1997; Toscano et al. 2005; Chucinta et al. 2000; Rogge et al. 1993). Moreover, Batonneau et al. (2004) identified $PbSO_4$, ZnS and CdS as the major phases generated by non-ferrous smelting operations. In addition, Cong et al. (2007) have shown that these metals might be long-range transported by atmospheric circulation. Consequently, their precise source might not be traced using only plain trace element geochemistry, so that isotopic research programs seem to be necessary to determine the origin of the metals (e.g. Grousset and Biscaye 2005; Dolgopolova et al. 2006).

In Santiago, S has a high EF_S at both sites. A lack of a good correlation between S and Cu or Zn (Table 3) precludes S being a primary sulphide phase. S appears more likely in sulphate phases, as demonstrated by the SEM–EDX study. Its probable origin could be related to the copper mining industry, which constitutes the most significant source of ambient SO_2 in central Chile (Gallardo et al. 2000). Indeed, in central Chile, three industrial copper smelters emit >3 tonnes of sulphur per day (García-Huidobro et al. 2001). However, two mathematical models by Gallardo et al. (2000) and García-Huidobro et al. (2001), respectively, reached contradictory conclusions concerning the impact of these smelters on the S budget of Santiago. According to García-Huidobro et al. (2001) SO_2 concentrations in Santiago area are mostly controlled by local urban and industrial emissions, with sporadic contributions from the copper smelters. On the other hand, Gallardo et al. (2002) and Olivares et al. (2002) argued that a high contribution from one of these three Cu-smelters (namely Caletones) is present in the Santiago basin. We support an origin related to the copper smelters for S, because of the very high EF for Cu and Zn in Teatinos, and for Zn in Macul. However, due to our limited sampling, we cannot prove one or the other model.

Finally, the anomalously high Cl content is probably not due to NaCl from marine salts, because very few NaCl grains were observed during the SEM study. Unfortunately this direct observation cannot be confirmed as the Na content of the samples is unknown. Nevertheless, the origin of Cl is probably anthropogenic and related to industrial emissions. This aspect will have to be confirmed by further studies.

Conclusions

This preliminary study focussed on some major element chemistry and particle identification showed that these two tools, even if imperfect, yield valuable information on the solid particles and chemical elements present in the air of Santiago. Besides the contribution of carbon particles, which can be quite important, especially downtown, unambiguously lithogenic particles and elements are the second highest contributors. Major element and particle identification together with magnetic properties show that the origin of disputable particles, such as iron oxides, is mostly anthropogenic magnetites. Enrichment Factors together with particle identification and element correlation indicate anthropogenic origins that are specific to the Santiago area.

However, accurate data on metal concentrations are needed to obtain a clearer insight into the cause of medical diseases in relation to chemical components. Indeed, it should be kept in mind that even lithogenic particles can transport (through adsorption or reaction processes) chemicals, including toxic metals. Therefore the toxic metal content of these particles, in relation to their size, type, sample date, location, etc. will have to be measured. Moreover, as small particles are richer in anthropogenic compounds, high-resolution techniques (TEM and FEG–SEM) are necessary to understand the mineralogy and chemistry of the $<PM_{2.5}$ fractions.

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3.4 Mineralogical characterisation of the samples studied in geochemistry. La Paz and Las Condes samples from 2004/2005.

The study realized in Toulouse with JEOL JSM 6360 LV SEM on ~500 particles, from four pairs of PM2.5 - PM10 filters, three from La Paz and one from Las Condes. The sampling was on august, 3, 2004 for $F_1$1007-$F_3$1008 and $M_1$1011-$M_3$1012 (03/08/2004). Filters ($F_1$0971-$F_3$0972) and ($F_1$737-$F_3$738) have been collected in La Paz on June, 20, 2004 and August, 2, 2005, respectively. In total we analyzed 523 particles, 352 in the coarse fractions and 171 in the fine ones.

Through the EDS spectre for each particle identified in a given sample some mineralogical phases was interpreted and the principal conclusion are consitente with those presented in Morata et al, 2008:

- The percentage of lithogenic minerals varies but currently is highest in PM10.
- The metallic elements (Cu, Fe, Al…) usually are in PM2.5 and some of them present spheric forms related to process of high temperature.
- The specific study of this investigation from the resultants obtained from La Paz and Las Condes will be treated subsequently.

We analyzed four pairs of PM2.5 - PM10 filters, three from La Paz and one from Las Condes. We also analyzed a pair of filters from each station collected the same day: on August 3, 2004, i.e. samples $F_1$1007-$F_3$1008 from La Paz and $M_1$1011-$M_3$1012 from Las Condes. Filters ($F_1$0971-$F_3$0972) and ($F_1$737-$F_3$738) have been collected in La Paz on June, 20, 2004 and August, 2, 2005, respectively. In total we analyzed 523 particles, 352 in the coarse fractions and 171 in the fine ones.
As already mentioned by Morata et al. (2008), filters from downtown Santiago (La Paz here) present a black organic carbon coating, while at Las Condes filters are grey (as in Macul, Morata et al. 2008). This difference is consistent with the contrasting traffic intensity between these two areas.

3.4.1 Morphological Characteristics

The particles observed on a PM10 filter (F3-972), can appear as agglomerates (fig 1 and 2) or as individual grains with diameters between 5x4 µm (fig 3 and 4) to 6x5 µm (fig 5). In addition, it is possible to see spherical particles with diameter that varies between 2µm (fig 6 and 7) to 7x5 µm (fig 8). As said before, even though there was some analytical restriction, chemical compositions of particles allowed recognition of silicate phases. In some case the spectrum were very clear while in other they could fit with various types of silicates. Unidentified alumino-silicates are classified as Al-Si, while Na-Al-Si and Ca-Al-Si associations are interpreted as sodic and calcic feldspars (fig 9). Crystals containing Na-Mg-Al-Si-Ca are interpreted as pyroxenes or amphibole (fig 10 and 11) if supported roughly by elemental ratios and crystal aspects, Mg-K-Al-Si as clay (fig 12) and Si-alone as quartz (fig 13 and 14). As in Morata et al. (2008), fine particles usually contain iron, copper, zinc, barium, calcium and lead. We interpreted Fe-rich and Ca-rich particles (with nearly no other elements) as Fe- oxide and calcite respectively (fig 15 and 16). Particles containing the Ba-S (fig 17) or Ca-S associations are interpreted as sulfates, and particles with Cu-Fe-S, Fe-S and Zn-S (fig 18) as sulphide phases, as these interpretations are the more probable.

X axis represents energy (eV) and the Y axis represents intensity of signal response for the entire spectrum.

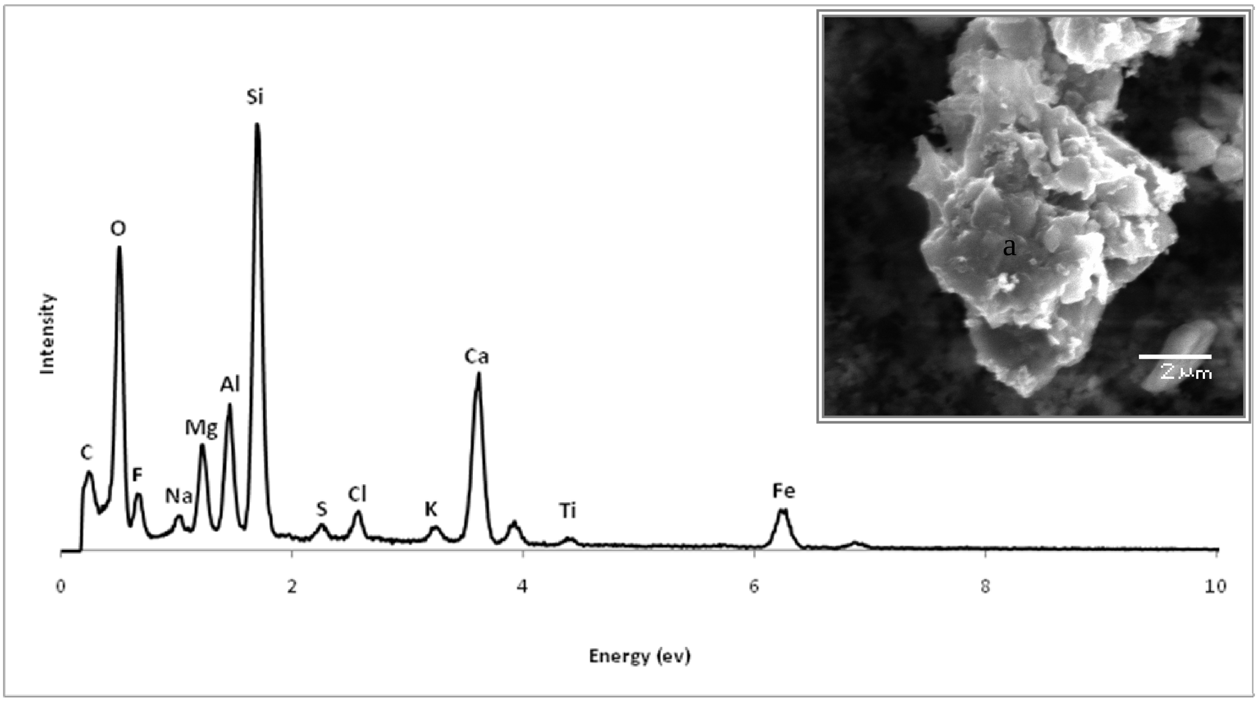

Figure 1: SEM Image of F3-972 sample. Date of sampling: 02/08/2004, PM10 from La Paz station. a) grain of Na-Mg-Al-Si-Ca-Fe ***(amphibole, pyroxene)****, fine layers with irregular surface, 6x6 µm.*

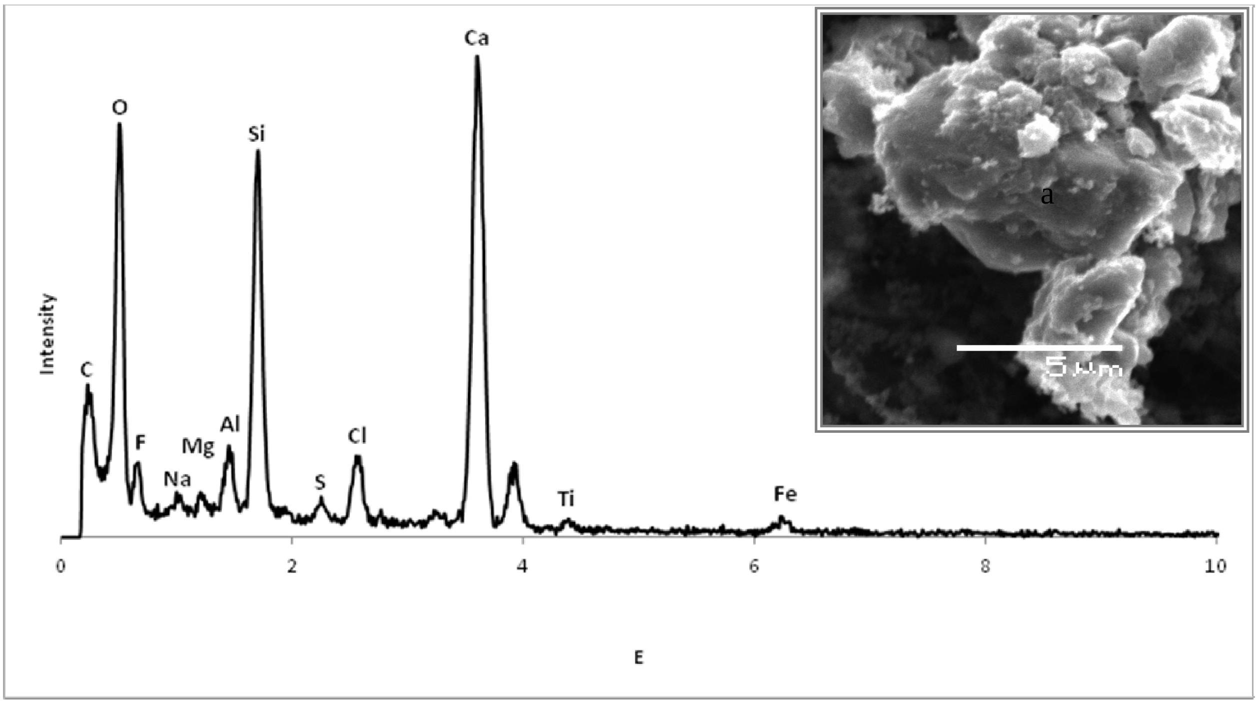

Figure 2: a) Agglomerate morphologies with mixing between Si-rich, Ca-rich, S and Cl.

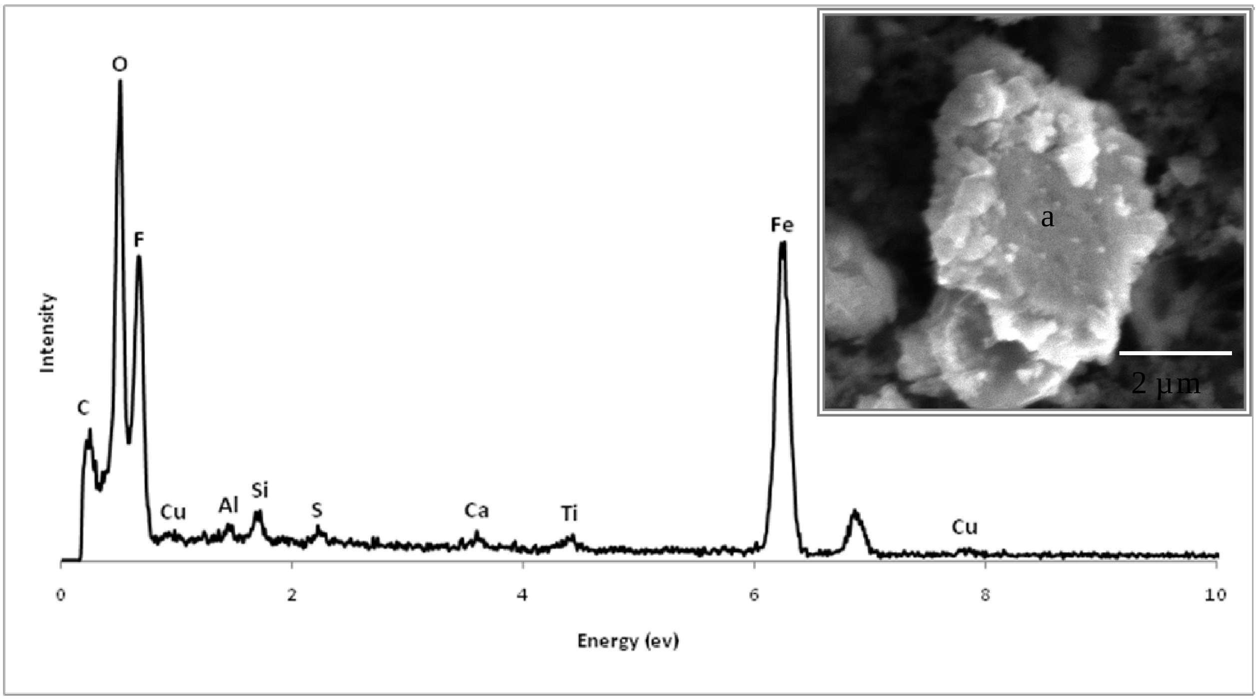

Figure 3: a) romboedric grain of Fe-rich, 5x5 um.

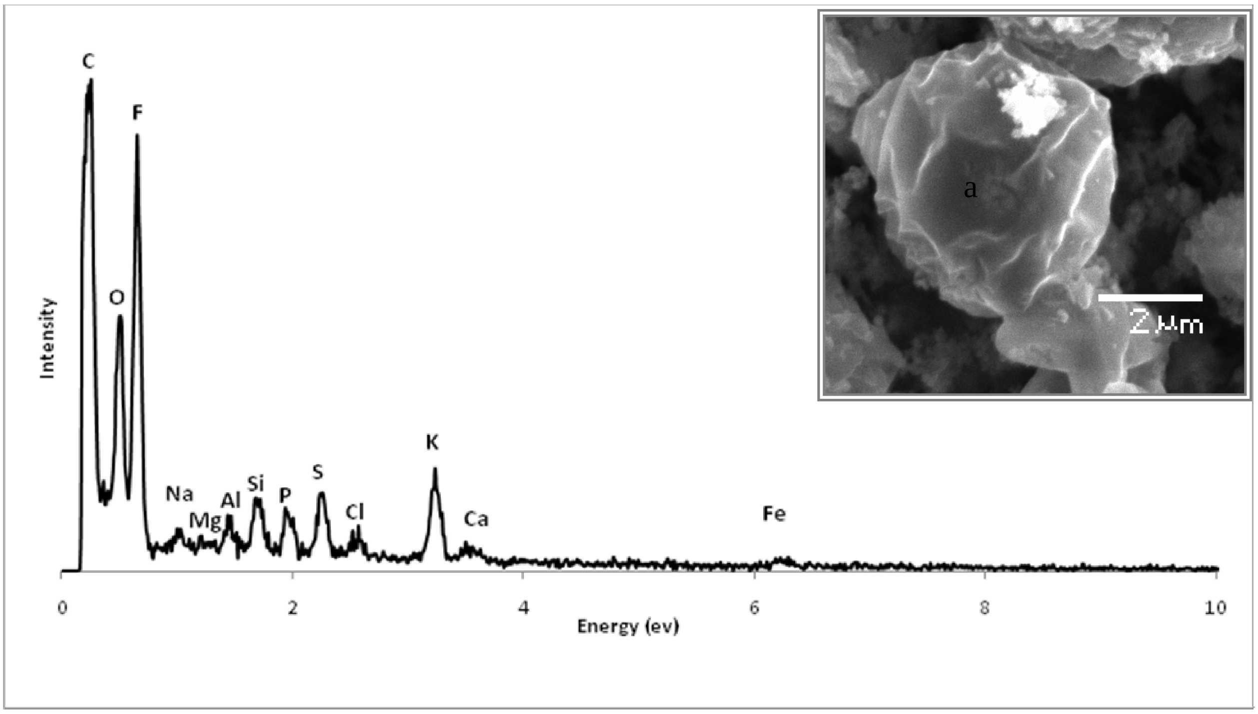

Figure 4: a) Mixing of: Na, Al, P, Si, S and Cl.

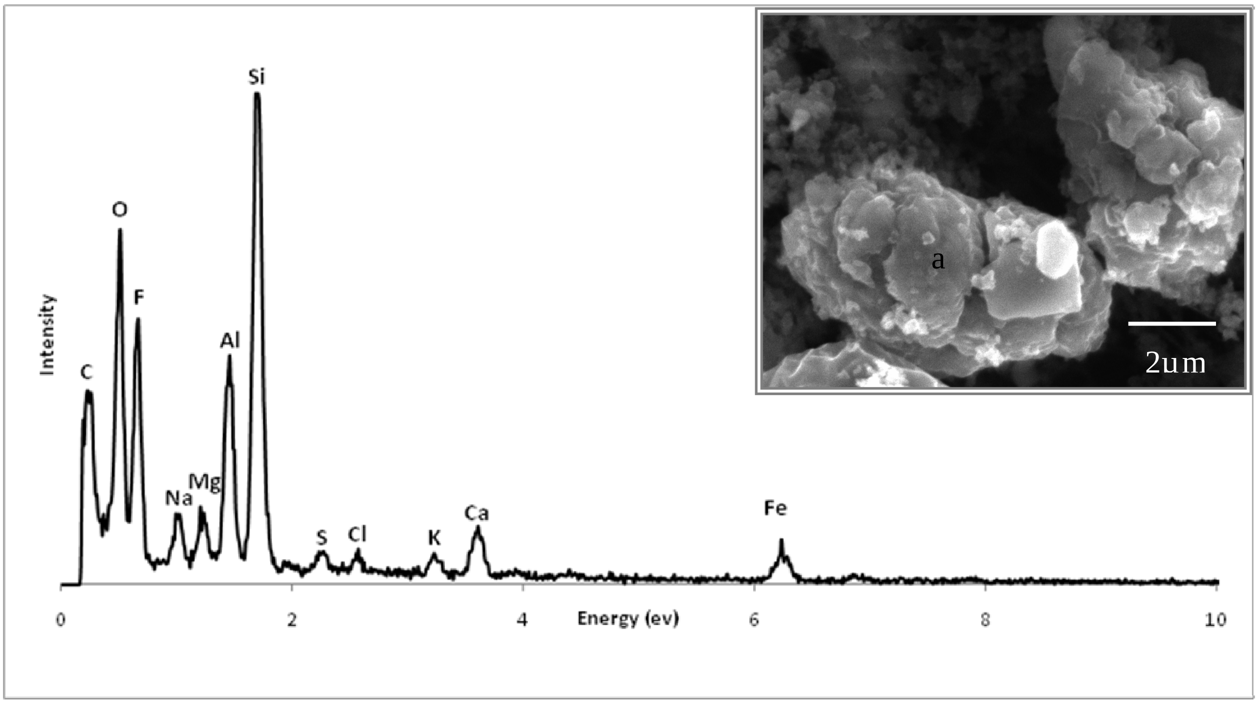

Figure 5: a) Na-Mg-Al-Si-Ca (pyroxene), S and Cl (fine layers).

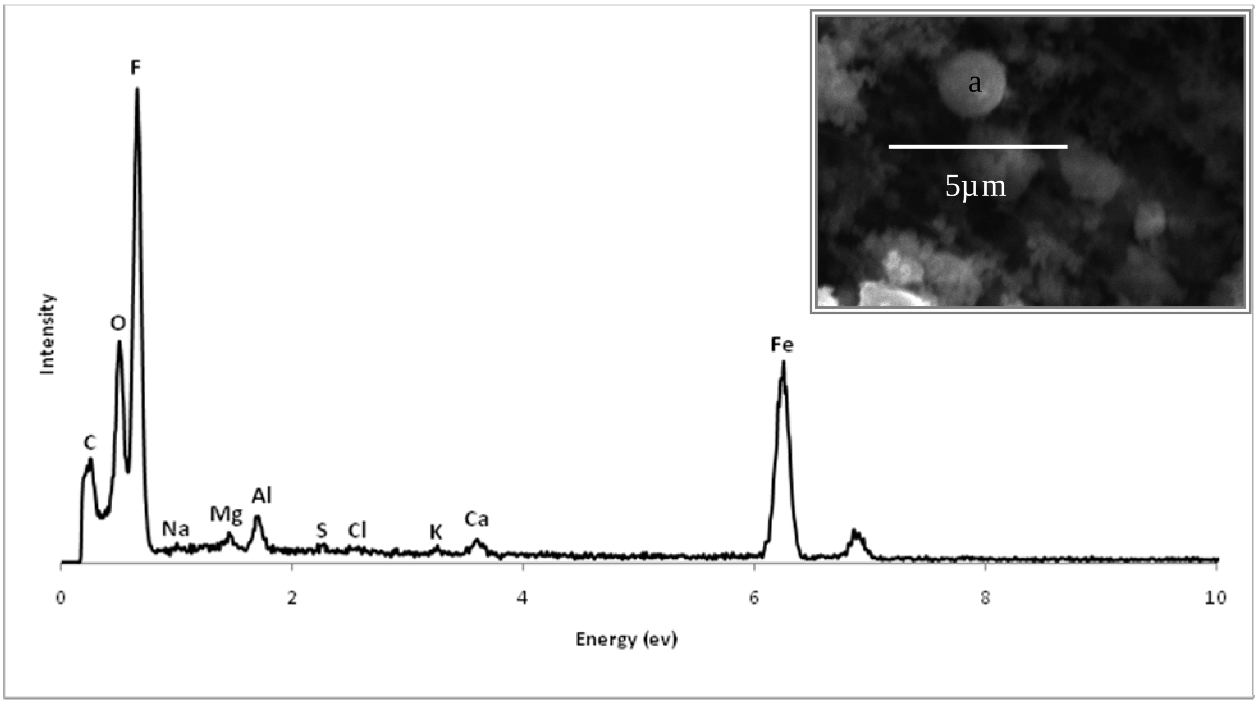

Figure 6: a) Fe-rich, spherical particle with 2 µm of diameter.

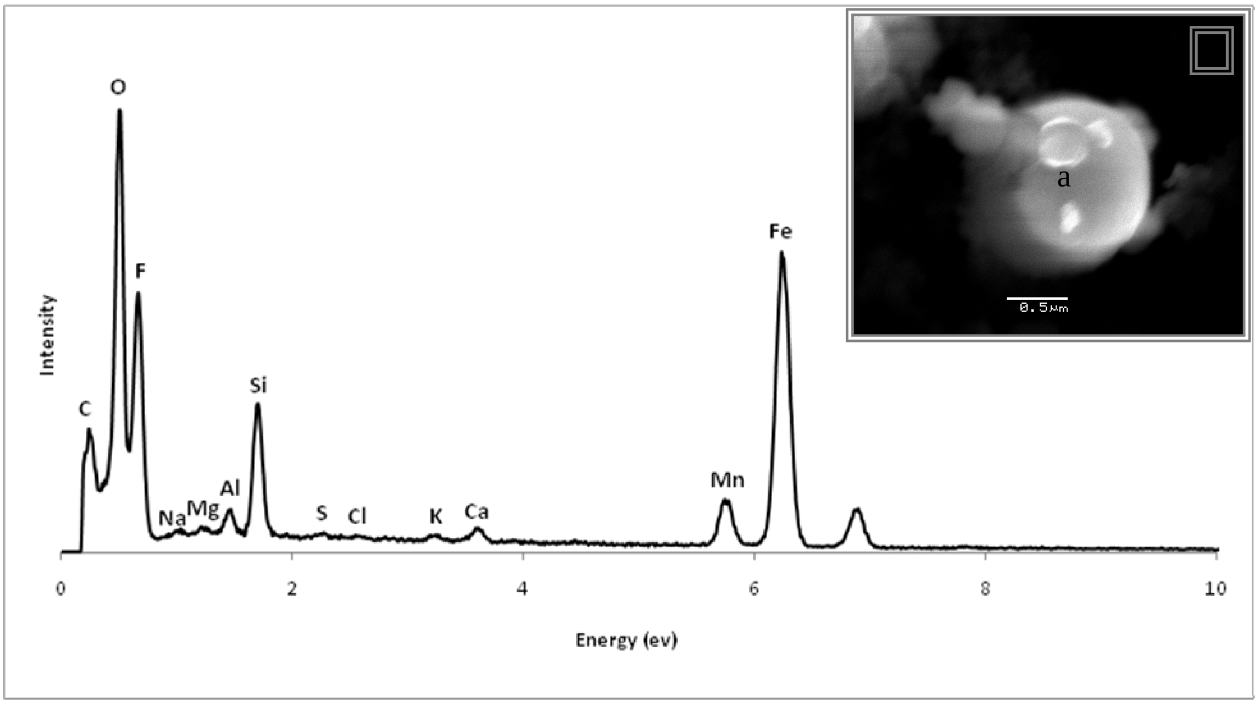

Figure 7: a) (Mn-Fe)-rich, Si-rich.

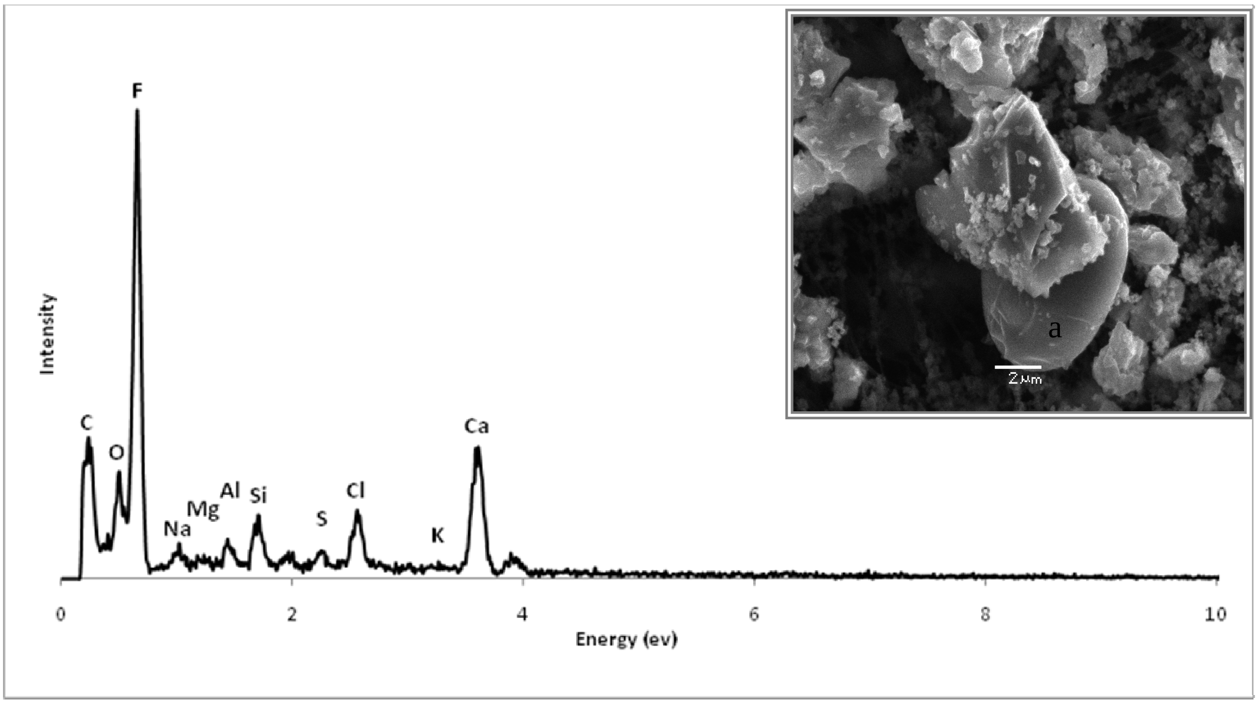

Figure 8: a) sphere (6x4 µm) with Ca-rich, S and Cl;

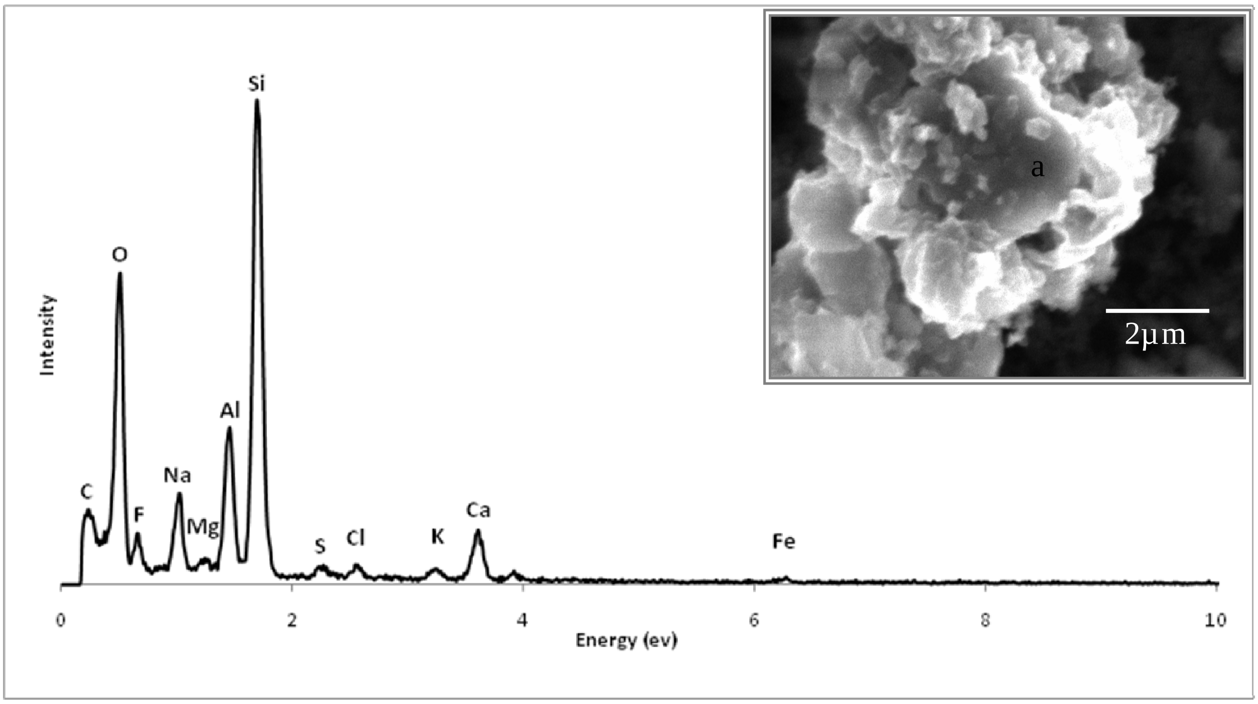

Figure 9: a) (Na-Ca)-Al-Si with irregulars borders and 3x3 um.

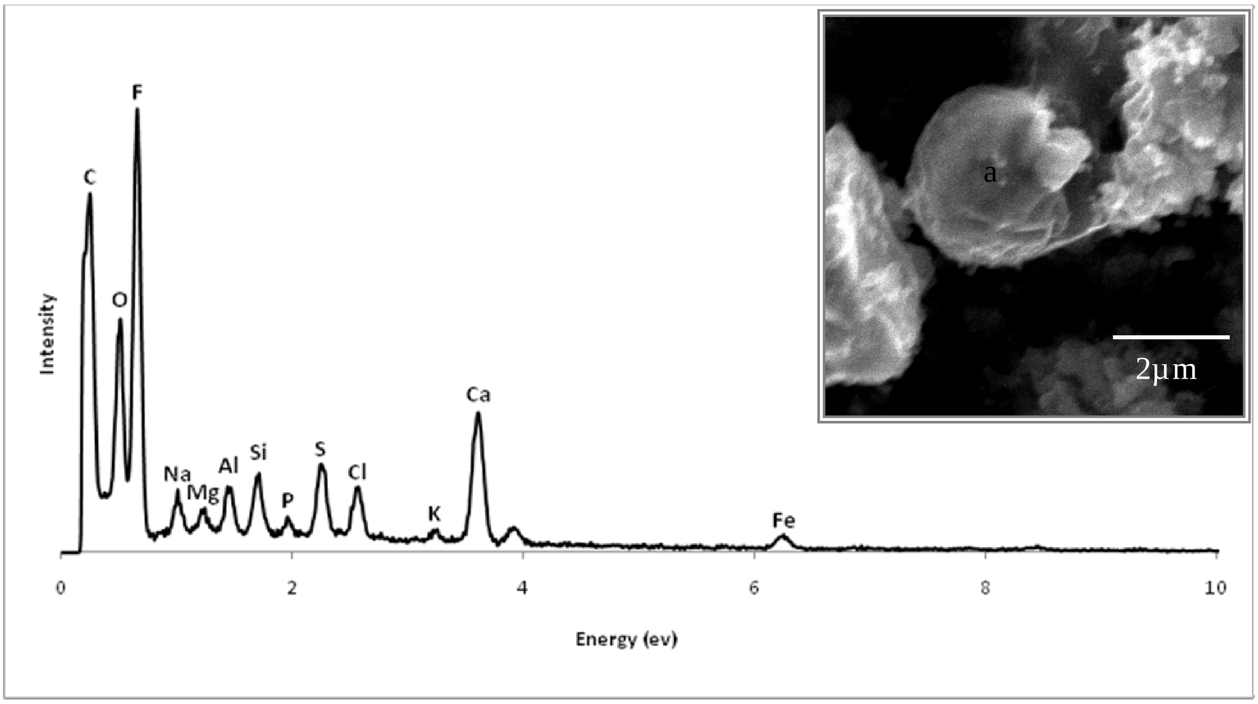

Figure 10: a) grain of Na-Mg-Al-Si-Ca-Fe ***amphibole****, S, Cl, 3x3 µm, with irregulars borders.*

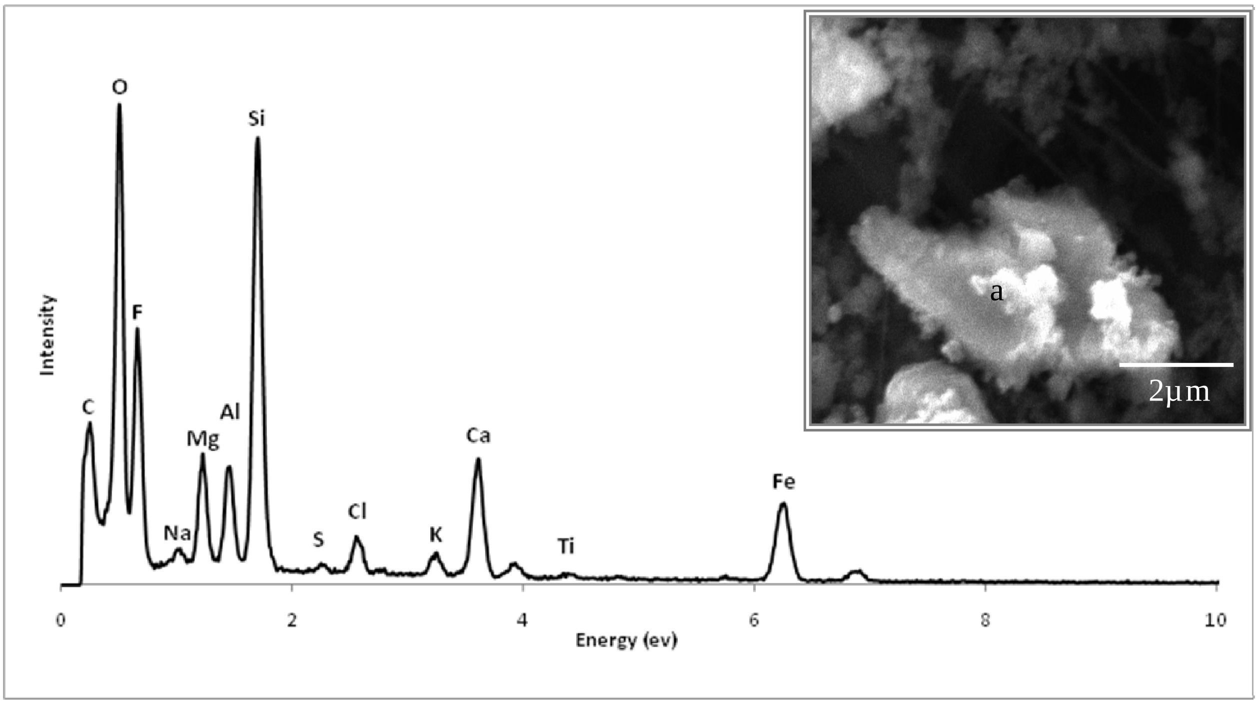

Figure 11: a) Na-Mg-Al-Si-Ca-Fe (amphibole).

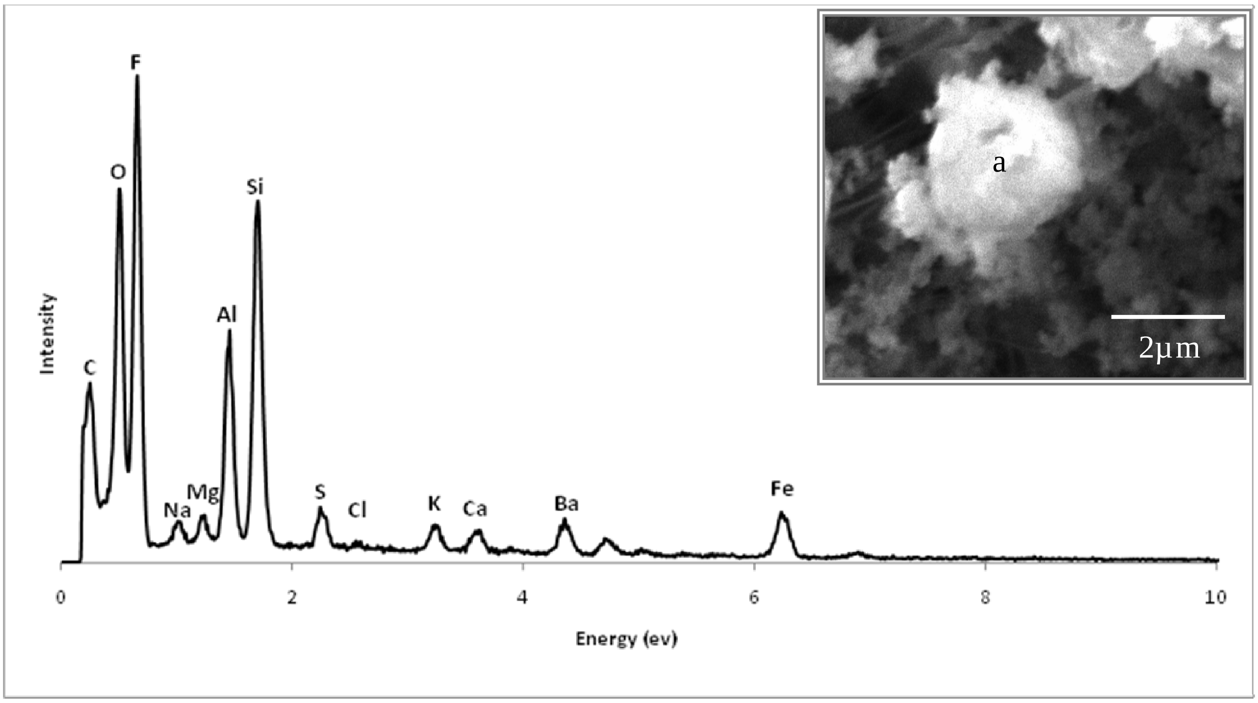

Figure 12: a) Ba-S, Na-Cl and Al-Mg-Si-K (Clay) S. rich

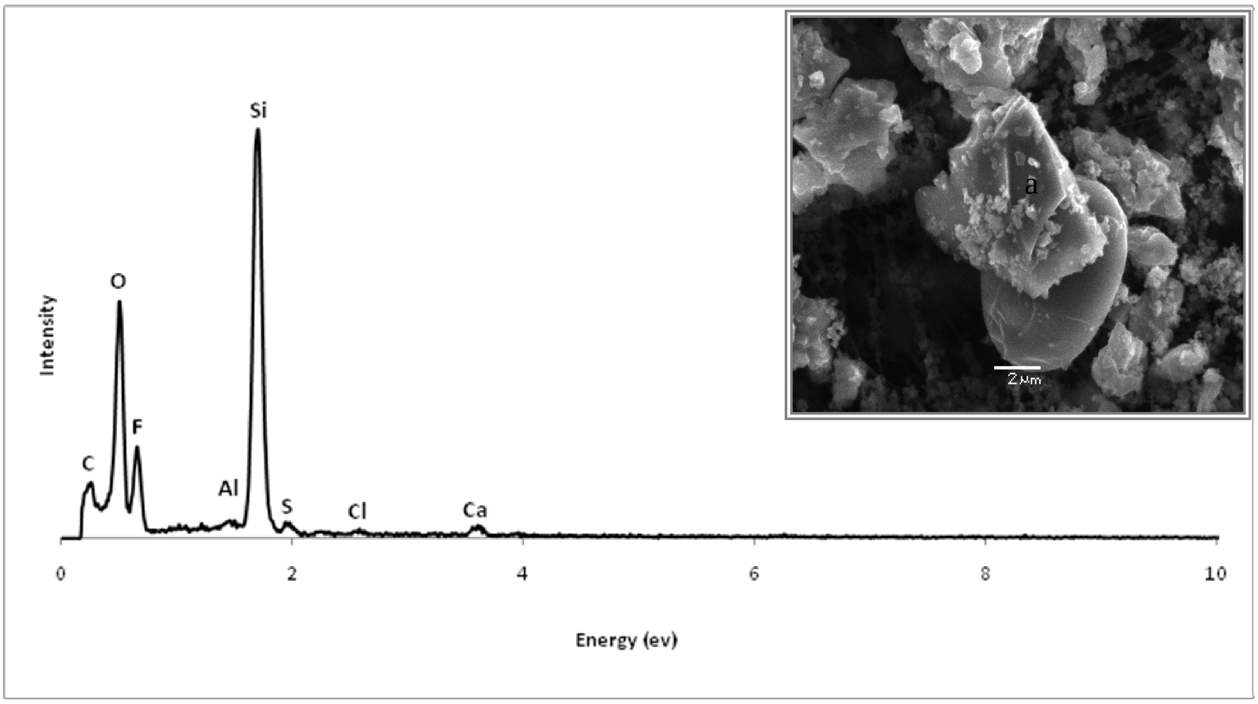

Figure 13: a) Si-rich 6x5 µm, with sharp borders

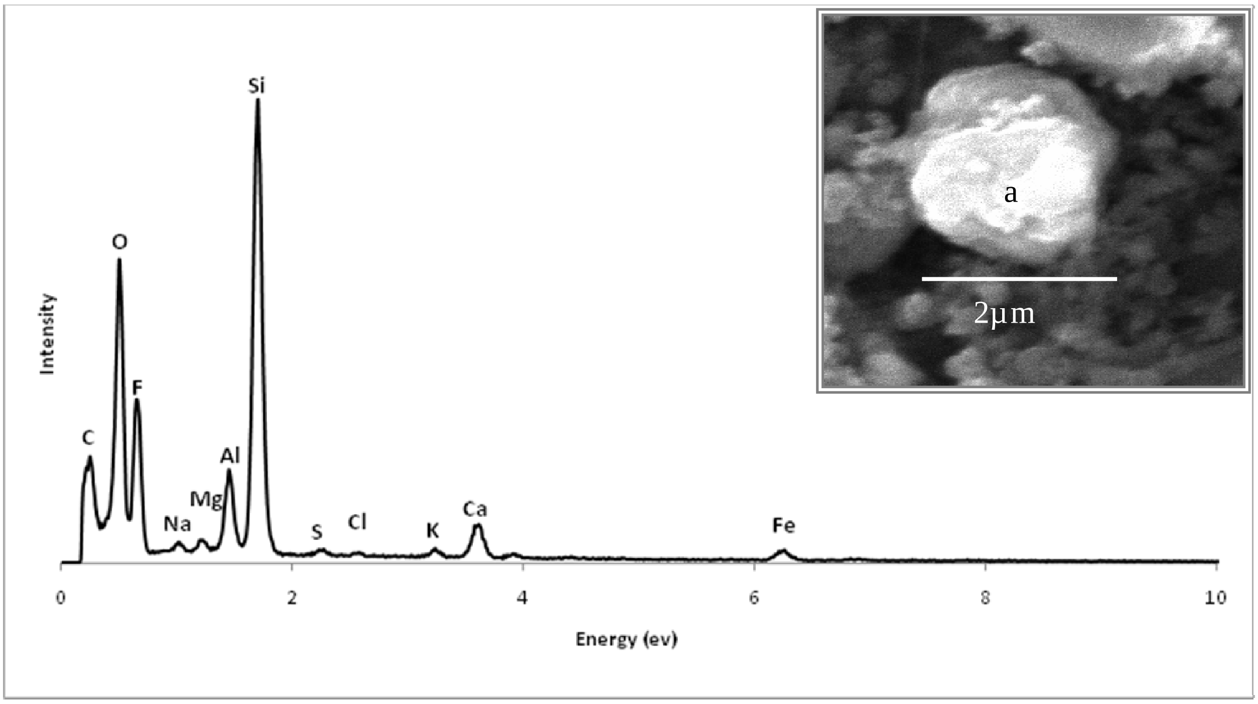

Figure 14: a) Si-rich.

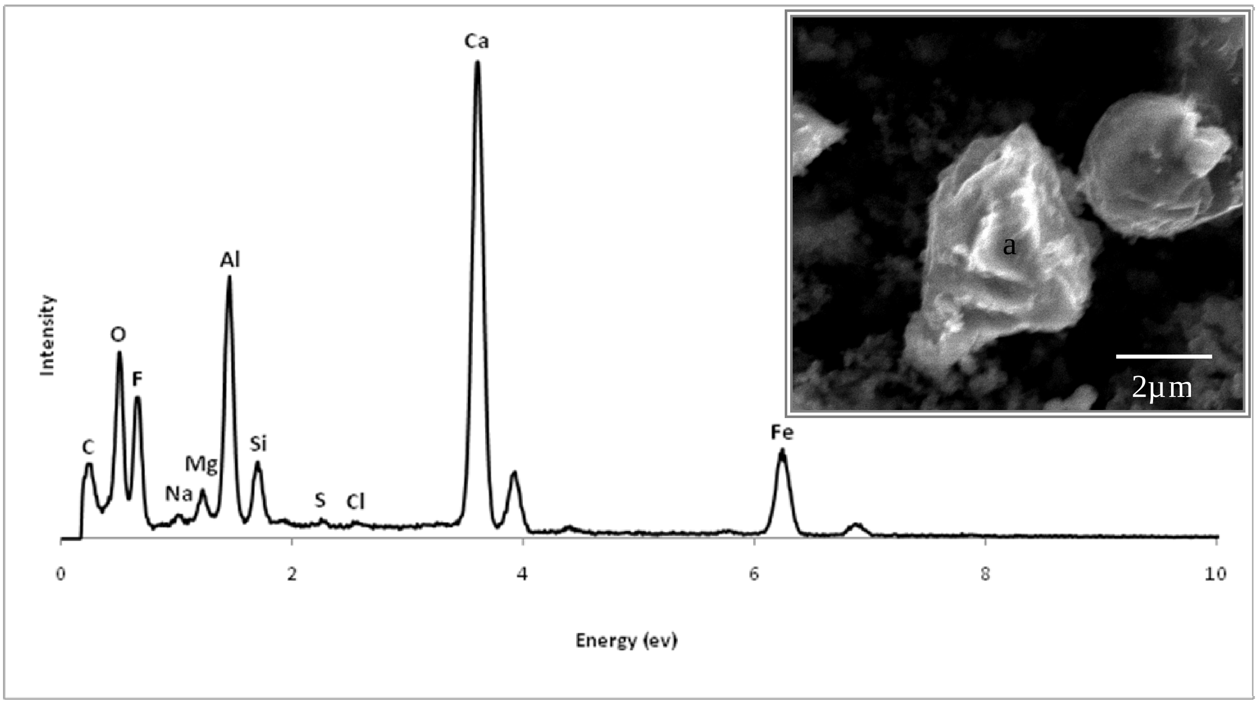

Figure 15: a) Ca-rich, Al-Si-Fe

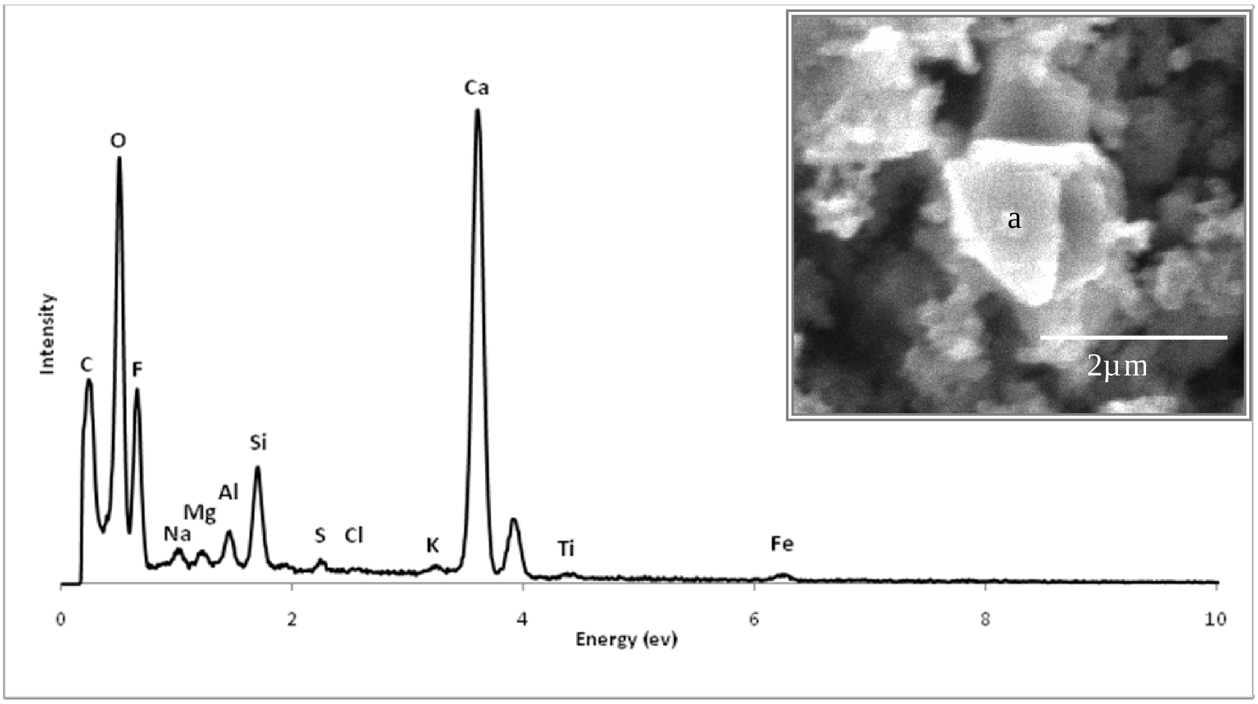

Figure 16: a) crystal of Ca-rich.

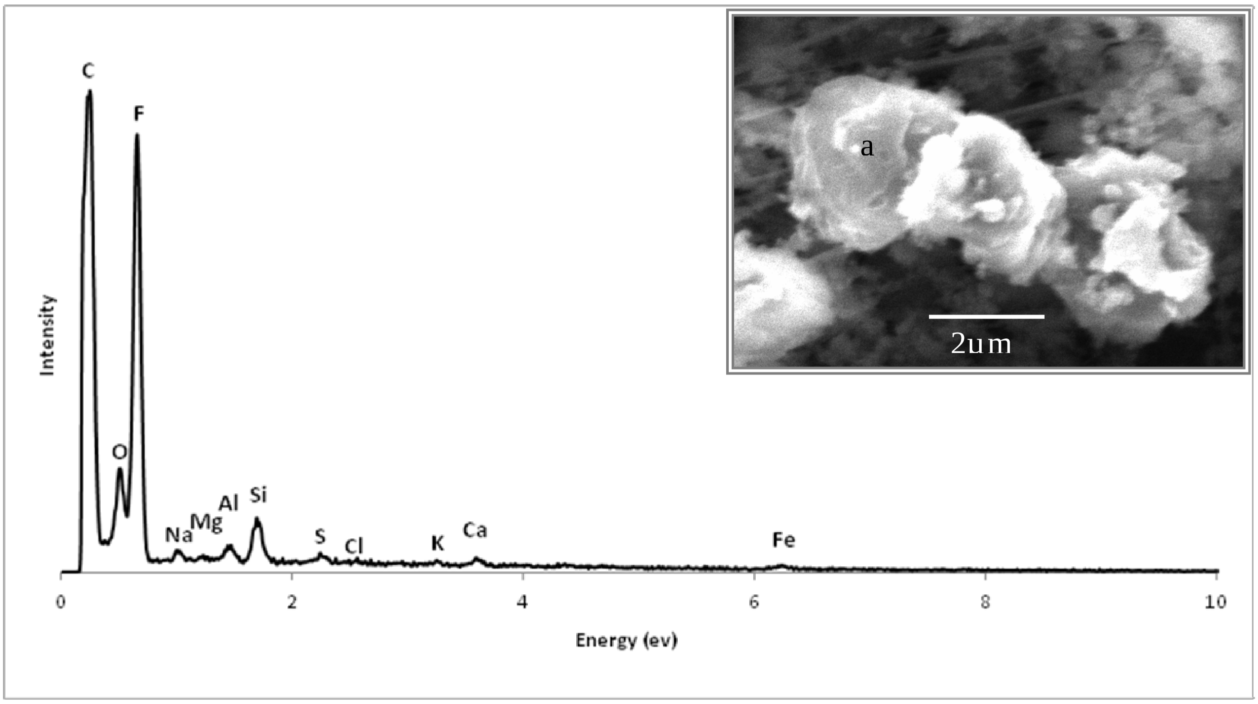

Figure 17: a) Al-Si, S, Cl.

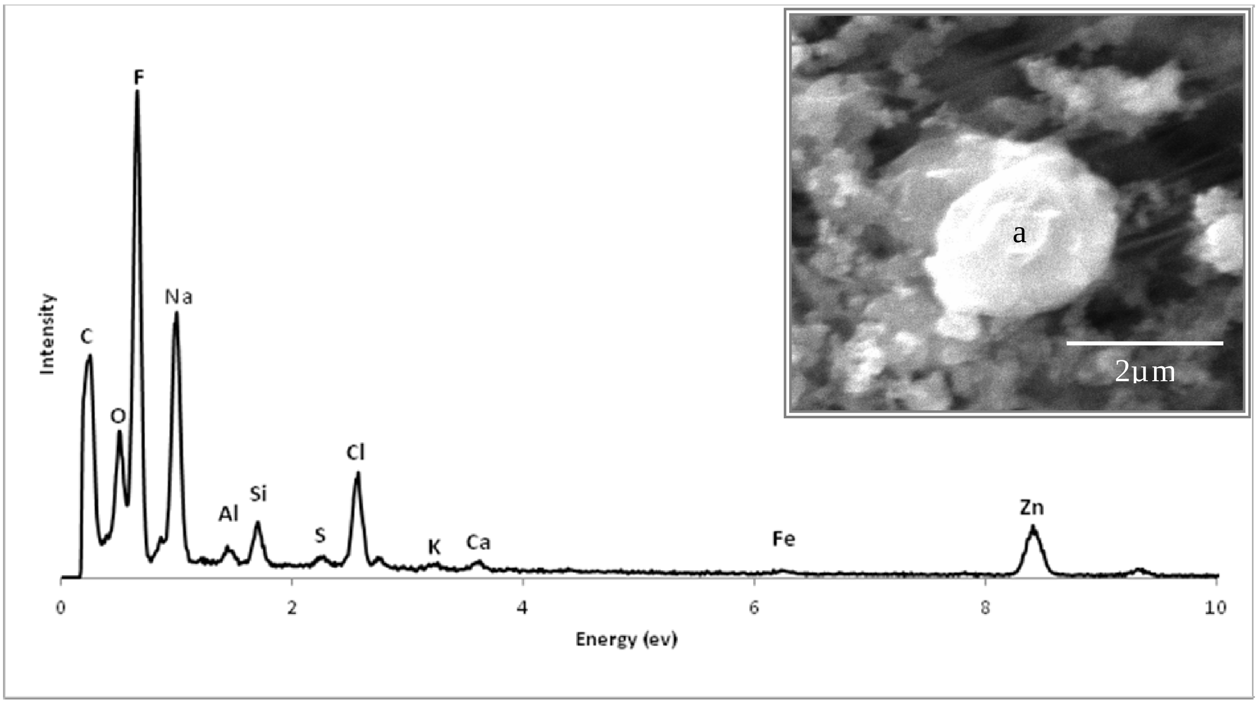

Figure 18: a) Zn-rich, S and Cl.

3.4.2 Comparison between La Paz and Las Condes

3.4.2.1 Major Contribution

In both stations (fig 19) the most frequently found associations are, in decreasing order: Al-Si, Si-rich (quartz), Na-Al-Si or Ca-Al-Si, Na-Mg-Al-Si-Ca, Na-Mg-Al-Si-Ca-Fe. All these associations, which correspond to different silicate phases, represent 75% (PM10) and 80% (PM2.5) at La Paz (fig 19a). Percentages are 75 % of all the PM 10 particles and 56 % of all PM2.5 particles at Las Condes (fig 19b). In addition, in Las Condes, contribution of pyroxenes-amphiboles (15% in PM10 and 10% in PM2.5) is higher than in La Paz (fig 19b).

All these associations could be interpreted as magmatic-derived minerals (Morata et al., 2008) Feldspar, pyroxene and amphibole due more represented in PM10 fractions than in the fine one. These observations are consistent with those already observed by Morata et al. (2008) at Macul and Teatinos. This behavior is consistent with the hypothesis that the main volcanic sequences (Abanico and Farellones Formations) around Santiago impact more in Las Condes than in central Santiago due to their relative geographic position. Indeed Las Condes station is more affected by the local breeze during the day due the down mountain wind from northeast during the night, bringing crustal material directly from the Andes.

Moreover, the surroundings of La Paz are all concrete and the streets are paved, which diminishes the natural source for dust.

3.4.2.2 Minor contribution

At La Paz station 25% of the total PM10 are represented by the following associations: Si-Al-Mg (possible clays), Fe-rich, Ca-rich, Alkaline-S, Ba-S and usually some possible sulfate phases such as Cu-Fe-S, Fe-S and Zn-S, are more important in PM2.5 fractions (fig 19a F11007). In some cases these associations can be observed in 40% of samples dated 20/06/2004 (F1737) and 02/08/2005 (F1-0971) at La Paz station (fig 21).

The presence of S and Cl is observed as Pb-Cl (fig 22), Pb-S and Zn-Cl (fig 18) associations (sample: F1-1007 (03/08/2004)), is acknowledge, but their contribution is statistically negligible (one or two particles per analyzed sample) and have therefore not been included in calculations.

Fe-rich (oxides)

Figure 19 shows that Fe-O association in PM2.5 is far more frequent (27%) in Las Condes than in La Paz (4%). Two types of Fe-O associations can be found, which correspond to different size and shapes. The first category 2µm in size has non characteristic, anhedral morphologies over. The second category present diameters < 1µm (fig 20), often associated with spherical morphology.

Figure 20 shows the histogram of the average sizes of these particles (51 in total), showing the relationship between percentage of distribution and diameters of each mineral phase. Particle diameter distribution in PM2.5 and PM10 corresponds to nucleation or condensation range (1nm-1um) and accumulation range (0.1-2 µm), respectively (Seinfield and Pandis, 1998). The origin of heavy metals fine particles is considered to be formed and emitted during combustion or industrial smelting process at high temperature (Sandoval et al., 1993; Morales, 2006). In fact, these metals can exist as a solid and gaseous phases (Desboeufs, et al., 2005). In addition, the residence time of these particles in the atmosphere is between 1-10 days (Seinfield and Pandis, 1998; Posfai and Molnar, 2000), during which they can be fixed by adsorption in preexistent particles. Therefore, and according with all of previous antecedents, a potential origin for these Fe-rich particles is combustion and/or smelter process, while Morata et al. (2008) attributed a traffic origin for the spherical particles and a lithogenic origin for the badly crystallized larger Fe rich particles.

Fe-S, Cu-Fe-S, Pb-S

The presence of particles with Fe-S, Ba-S (fig 23), and Cu-Fe-S (fig 24) and Pb-S (fig 25, sample: F1-1007) also has been noted. According to their percentage of contribution and the variation of diameters from 0.5 to 1.5 µm for Ba-S and 2 to 2.5 for Ca-S, the growing time estimated for both minerals has been considered between l to 10 days (Seinfield and Pandis, 1998), time necessary for some chemical reaction between ion Ca++, Ba++, Na+, K+ and S-. Previous authors (Sandoval et al., 1993; Morales et al., 2006) has been considered sulfate formation as products of SO_2 oxidation in presence of Fe and Mn. Therefore, the presence of these chemical compositions (Ca-S and Ba-S) allows to suppose the existence of gypsum and barite. On the other hand, gypsum can also be related with quarries and plaster industry. While Pb-S could be generated by oxidation of PbS, the rest of particles could be related with double decomposition with one phase solid formed. On the other hand, the presence of SO_4 has been described by Gallardo et al. (2002) who showed some evidence of an enhanced contribution of Caletones, the largest copper smelter in the area, to the load of SOx in the Santiago basin, especially in the form of sulphate associated to fine particles (diameters < 2.5 mm) Gallardo et al. (2002).

NaCl

At Santiago de Chile the mass of air related with advection process brings NaCl. The presence of Na and S in some particles (fig 26) is probably related with a secondary formation. Therefore, one potential source for Cl could be related with sea aerosols. Nevertheless, the origin of Cl^{-1} could be formed from solution with high concentrations of chloride at high temperatures. This origin is probably related with industrial processes (Morata et al., 2008).

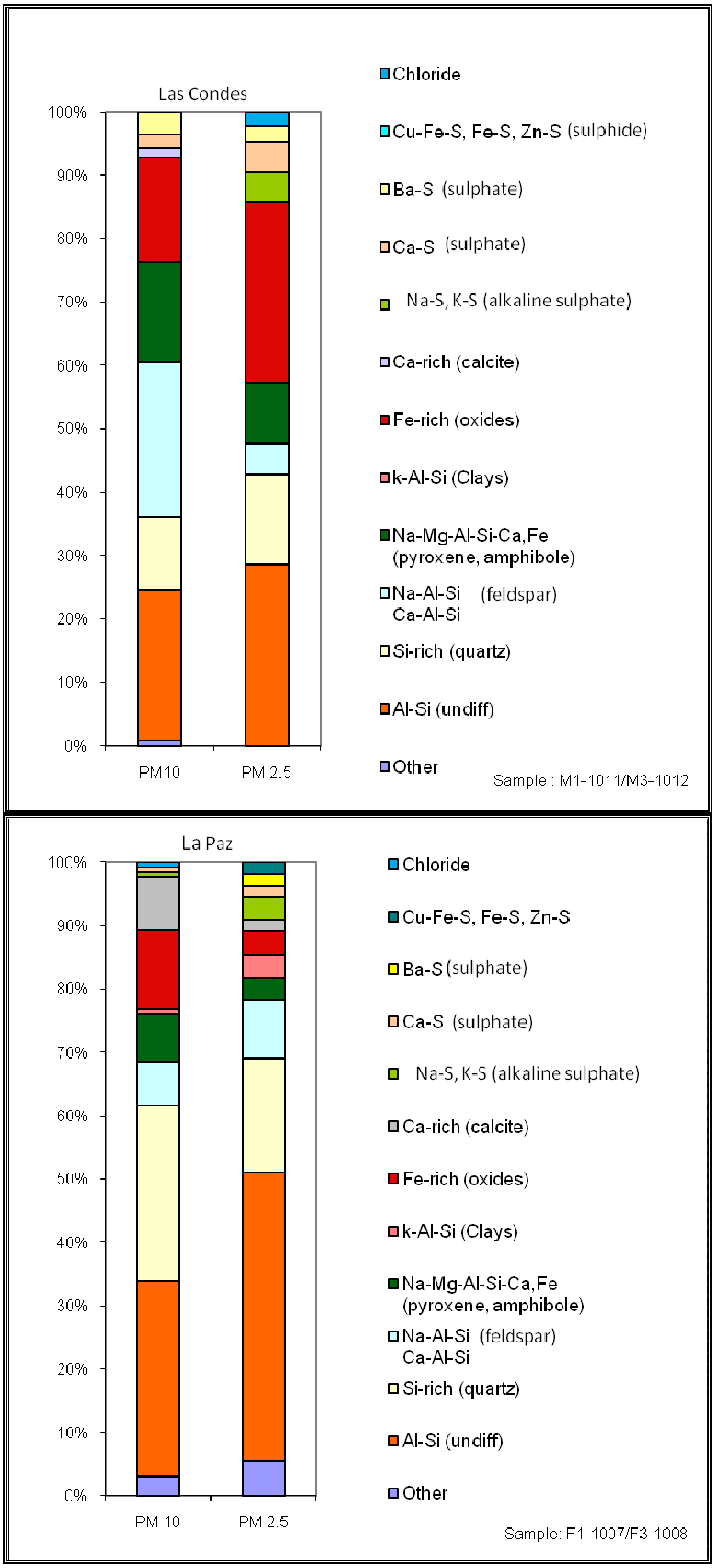

Figure 19: Percentage of contribution of minerals determined from analysis with SEM. Date of sampling: 03/08/2004. The analyzed samples are: $F_1$1007 (PM2.5)-$F_3$1008 (PM10) and M_1-1011 (PM2.5) - $M_3$1012 (PM 25), from La Paz (above) and Las Condes stations (below), respectively. The percentage was calculated on 55 particles in PM2.5 and 130 particles in PM10 at La Paz. At Las Condes it was calculated on 42 (PM2.5) and 143 (PM10). F11007 are: Fe-S, Zn-S, Fe-Cu-S; Pb-S, Pb-Cl.

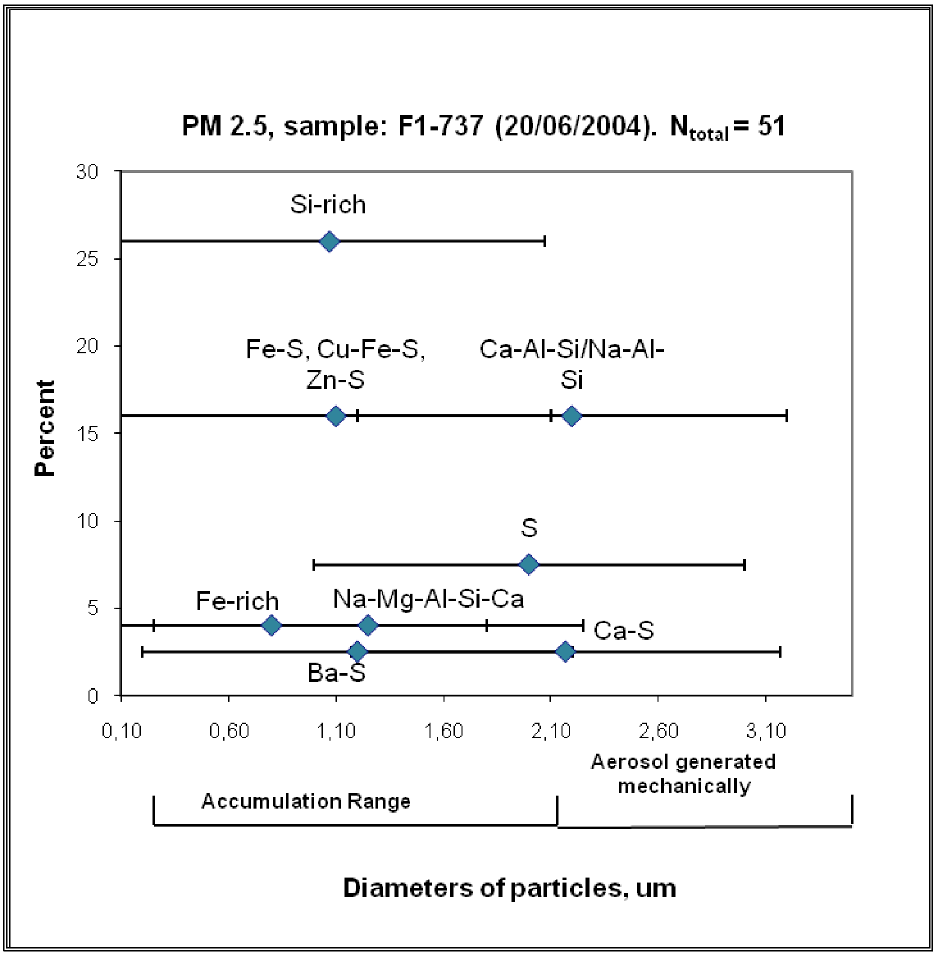

Figure 20: Percentile distribution and corresponding particles diameters determined from SEM analysis (20/06/2004). The analyzed samples are $F_1$737 from La Paz. The percentage and diameters of particles were calculated on 51 particles in PM2.5. Na-Al-Si and Ca-Al-Si presents a high diameter while Fe-rich present smaller particles. Accumulation and mechanical generation classifications are based in Morales et al., 2006.

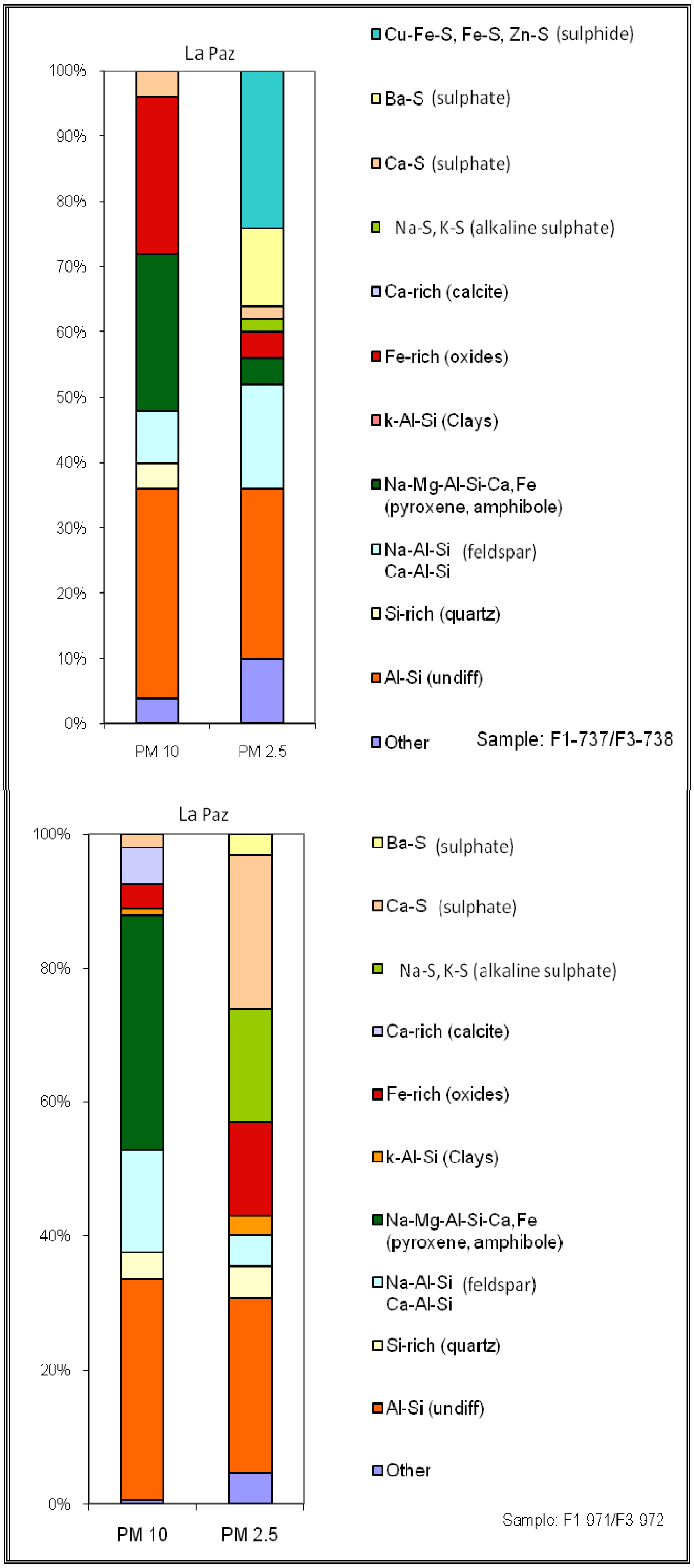

Figure 21: Percentage of contribution determined from analysis with SEM. Date of sampling: 20/06/2004: samples F$_1$737-F$_3$738 (above) and 02/08/2005: samples F$_1$0971-F$_3$0972 (below). In 2004, the percentage was calculated on 51 particles in PM2.5 and 25 particles in PM10, while in 2005 on 65 (PM2.5) and 197 (PM10) particles. F$_1$737 are: Fe-S, Zn-S, Fe-Cu-S.

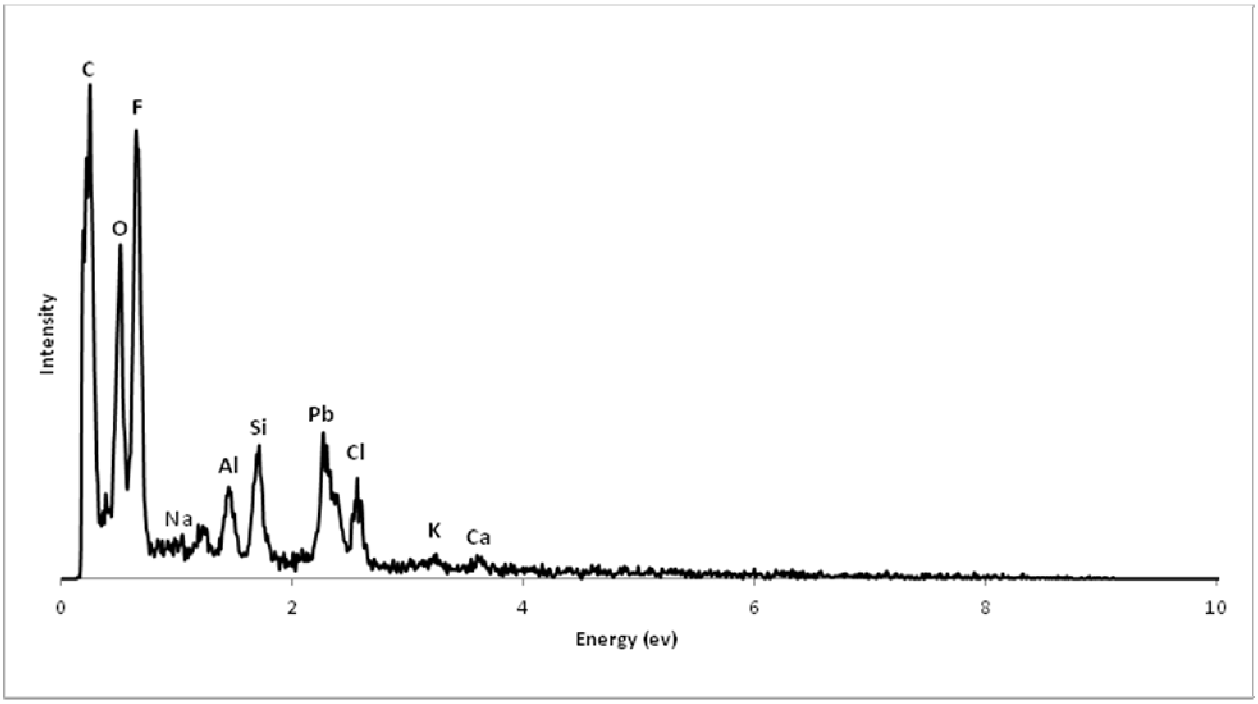

Figure 22: Observed association: Pb-Cl.

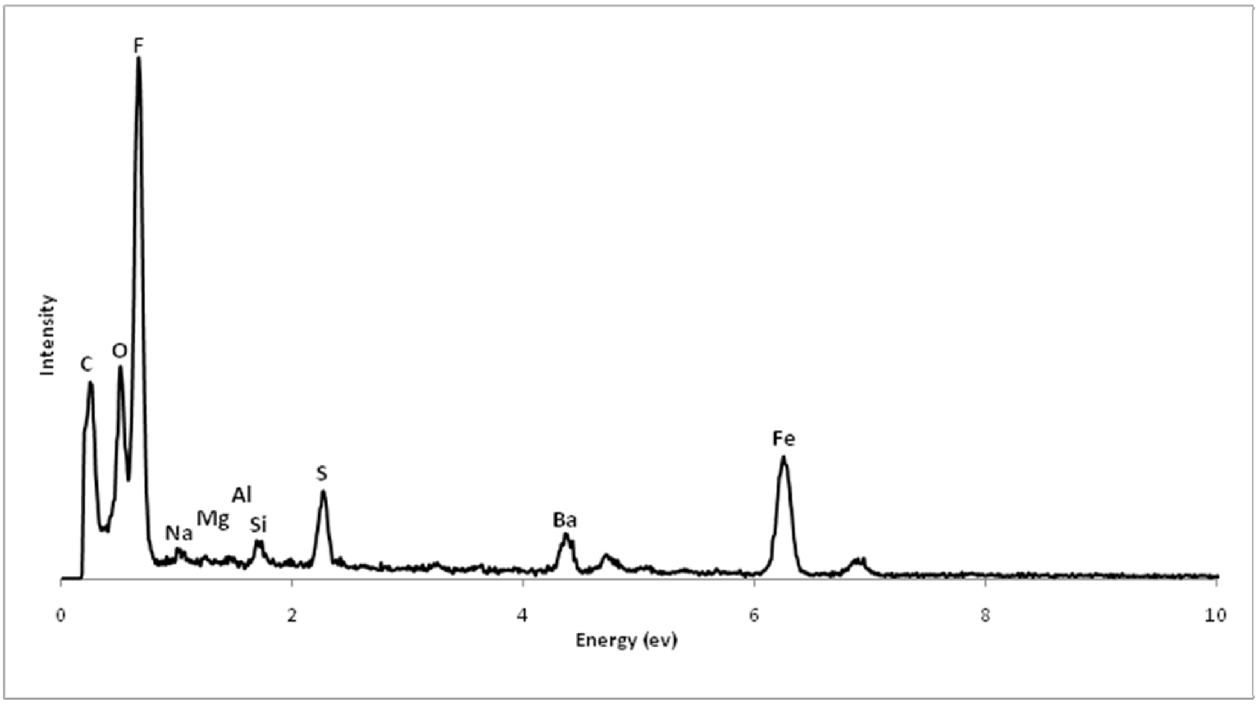

Figure 23: Observed association: Ba-S and Fe-S.

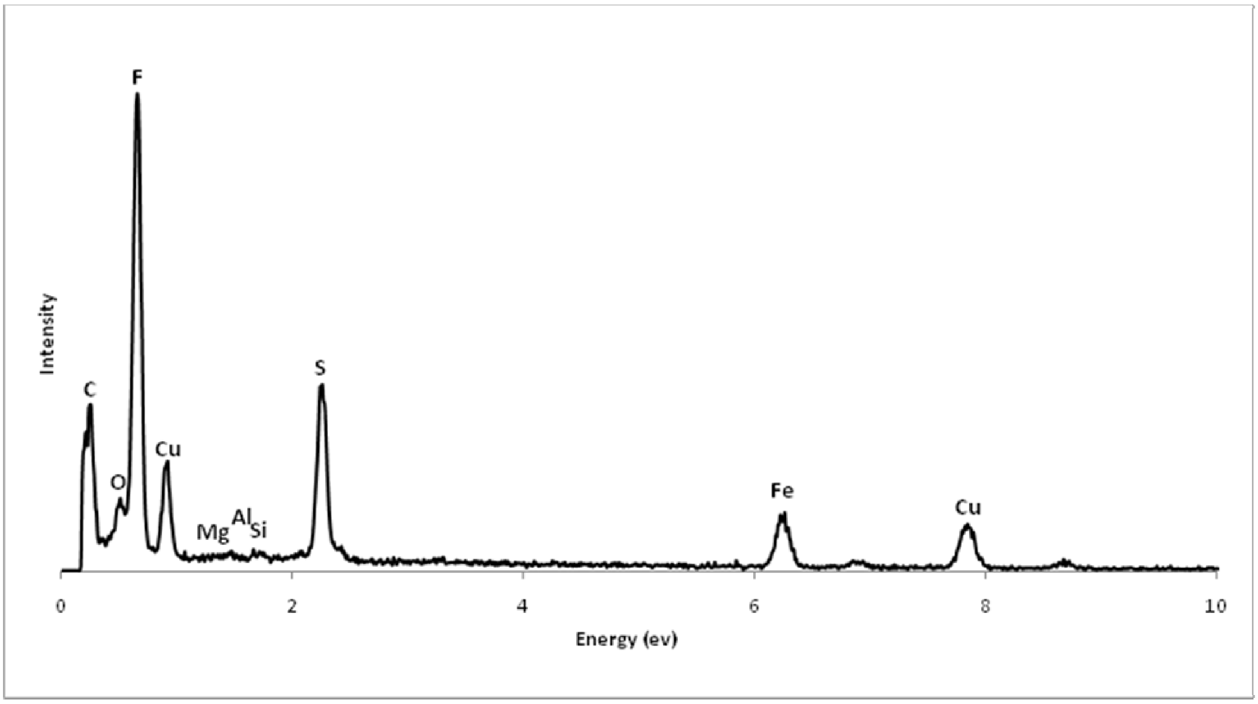

Figure 24: Observed association: Fe-Cu-S

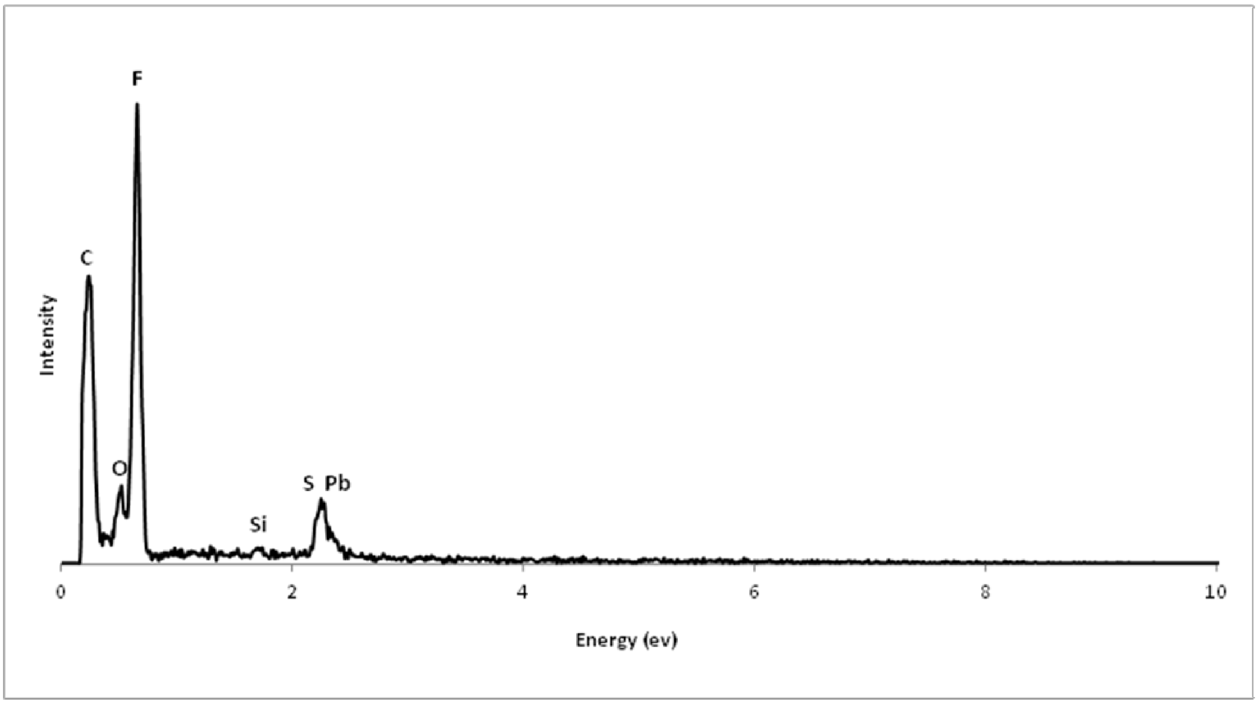

Figure 25: Observed association: Pb-S.

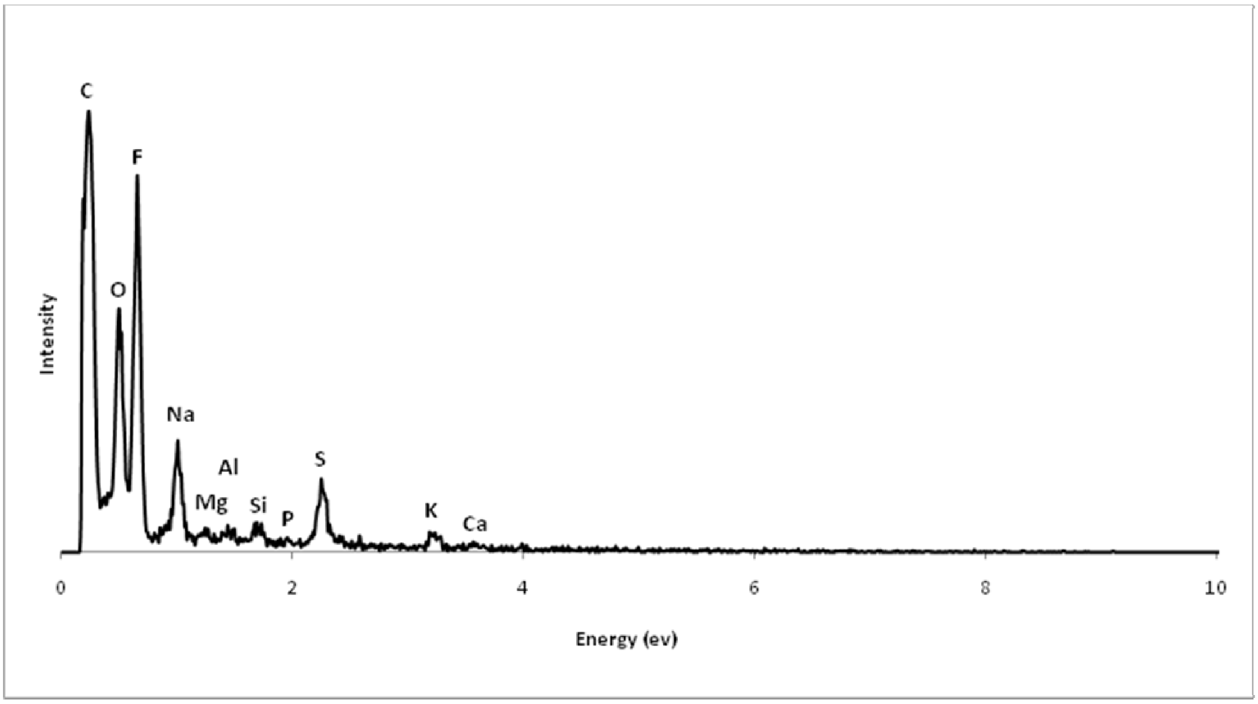

Figure 26: Observed association: Na-S.

3.4.3 Conclusion

The analysis of SEM applied on 523 particles allows the identification of the origin and geochemical process associated with physical parameters.

The major percentage of contribution is from alumina-silicates (probably feldspar-plagioclases, pyroxenes, amphiboles) and in most cases is associated with the coarse fraction and could have crustal origins. On the other hand, iron oxides, sulfate phases, sulfur and sulfides are mostly concentrated in the fine fraction. These observations were already described by Morata et al. (2008).

Morata et al. (2008) preclude S as a primary sulphide phase and explain its presence as principally related with sulfate phases, probably emitted by Caletones. According to previous studies (Gallardo et al., 2002 and Garcia-Huidobro et al., 2001) there exists more than one S emission source. According to Morata et al. (2008), in the present study we suggest that sulphide phases are related with copper smelting. In addition, we propose that sulphate phases form as secondary particles, but this does exclude the possibility that smelter emission do not also provide some contribution.

Based on our observations and those of previous studies (Sandoval et al., 1993), we support two or more anthropogenic sources for FeO (combustion or industrial smelting process).

Morata et al. (2008) also attributed these particles to anthropogenic origins (vehicular traffic) but also suggest that some origins of FeO could be in relation to lithogenic alteration of Fe-bearing minerals.

According to the smaller diameter in the FeO particles observed, we suggest that Fe is implicated in the formation of sulfate salts in the atmosphere.

During the SEM analysis the presence of Cl is almost constant. One of the potential sources for Cl is marine aerosols related with westerly winds that transport NaCl. This is also consistent with presence of Na during the analysis. The association of chlorides as a Zn-Cl, Pb-Cl and Cu-Cl could be as interpreted as a secondary formation.

CHAPITRE 4: GEOCHIMIE

4.1 Introduction

Comme indiqué dans les chapitres précédents, le matériel particulaire présent dans l'air de Santiago a des origines diverses. Dans un contexte régional et local, les activités industrielles ont un impact important, en particulier les activités minières, qui induisent l'accumulation de polluants dans l'air de la ville. D'autre part, la distribution et concentration de contaminants dépendent du climat et des caractéristiques physiques de Santiago.

A partir des années 1990, a commencé une politique d'amélioration de la qualité de l'air. Diverses études ont été menées afin de combattre la pollution atmosphérique. Pour poursuivre et affiner les ajustements de politique publique en termes de rejets à l'atmosphère, il est nécessaire de connaitre la nature du matériel particulaire et son origine pour mettre en ouvre mesures de réduction de la contamination adaptée. Les études de minéralogie ont permis de préciser la nature du matériel particulaire. Selon les résultats exposés dans le chapitre 3, il existe une importante contribution originaire de la croûte terrestre (~70%), normalement liée à la fraction majeure PM10, ce qui est cohérent avec les conditions topographiques, climatiques et géologiques naturelles de Santiago. Néanmoins les résultats montrent une contribution anthropogénique (~50%) qui s'exprime plus particulièrement dans la fraction fine PM2.5 et reconnue dans les stations placées au centre ville, qui sont plus impactées par ces sources anthropogéniques que les stations situées en domaine résidentiel.

Afin de compléter les résultats obtenus à partir des observations de minéralogie, en termes de caractérisation et quantification de la contamination et d'identification des sources, nous avons travaillé sur des sites qui présentent des caractéristiques urbaines similaires aux sites analysés dans le chapitre 3. Il s'agit des stations La Paz, située au centre ville et impactée par les usines et le trafic, et Las Condes localisée à proximité des Andes, dans un domaine plus résidentiel de Santiago.

C'est à partir de la moitié des années 1990 que les premières études de compositions élémentaires apparaissent dans le but d'identifier les sources de pollution à Santiago et d'évaluer les conséquences de la pollution sur la santé. Une décennie après, est apparu le besoin de posséder une base de données extensive sur les concentrations élémentaires des fractions fines et grossières du matériel particulaire, base de données qui concernerait un nombre élevé d'éléments chimiques et qui reposerait sur des séries temporelles longues, qui seules permettent de tracer l'impact sur la santé et de procéder à l'actualisation des sources d'émissions et des processus associés à la génération de matériel particulaire.

Les résultats obtenus à partir d'analyses par ICP-MS permettent de répondre à ces objectifs en utilisant des outils de traitement de données (facteur d'enrichissement, analyses de facteur, rapports de terres rares, corrélations avec les paramètres météorologiques) et à partir de la comparaison avec des données publiées antérieurement.

L'ensemble des résultats et des observations, réalisées dans les années 2004 et 2005 à Santiago du Chili, sont exposés dans le présent chapitre sous forme d'un projet de publication.

4.2 Résumé de l’article en préparation

L’objectif de la présente publication est l’identification des sources qui impactent la qualité de l’air à Santiago du Chili et des mécanismes qui contrôlent leur variabilité temporelle et spatiale. Ceci passe par l’analyse des concentrations en éléments majeurs et traces dans la fraction particulaire respirable ainsi que leur variations entre sites mais aussi saisonnières et interannuelles.

Les deux stations sélectionnées appartiennent au réseau de surveillance de la métropole (réseau MACAM). Il s’agit de la station La Paz, localisée au centre ville (soumise aux effets des activités industrielles et du trafic automobile) et de la station Las Condes, située à Santiago au pied des Andes, dans un quartier plus résidentiel que la Paz . 202 échantillons, prélevés durant les années 2004 et 2005, sont représentatifs, pour les deux sites étudiés, des jours les plus pollués et les moins pollués de chaque mois. Les fractions fine (PM2.5) et grossière (PM10) on été analysées par ICP-MS au LMTG, Toulouse, France. Les résultats montrent que les concentrations sont systématiquement plus élevées en hiver qu’en été, en relation avec les mauvaises conditions de ventilation régnant dans le bassin de Santiago durant cette période froide. De plus on constate que la pollution au centre ville est systématiquement plus élevée que dans les quartiers résidentiels.

Afin de discriminer entre origines lithogénique et anthropogénique, on utilise la notion de facteur d’enrichissement (FE) par rapport à la composition d’un croûte continentale andésitique moyenne. Les éléments qui présentent un FE<10 comme Mg, Y, Zr, U Sr, Ca, Ti, V, correspondant à une origine principalement crustale et ceux qui présentent un FE>10 comme Rb, K, Cs, Fe, P, Ba, Mn, Ni, Cr, Co, Zn, Sn, Pb, Cu, Mo, Cd, As, Ag, Sb ont une origine principalement contrôlée par des activités anthropiques.

Après avoir effectué cette première discrimination, on utilise l’analyse factorielle afin de caractériser et discriminer les différentes sources (surtout anthrogéniques) présentes à Santiago. Les sources polluantes identifiées à partir des associations élémentaires ont été vérifiées et comparées à celle reconnues dans les études antérieures. En conséquence, cette étude permet de compléter et d’élargir la liste des éléments traces qui caractérisent les principales sources polluantes à Santiago. On peut ainsi distinguer 5 sources principales: 1) source naturelle (lithogénique et marine) tracée par Al, Ca, Na, Mg, Fe et Ti, Sr, Zr; 2) fonderies de cuivre (Cu, Mo, As, Zn et Pb); 3) combustion de pétrole et charbon tracée par Ni, V, Cr ; (4) trafic automobile (Mn) et (5) combustion de biomasse (K and Rb).

Néanmoins, les origines de certains éléments (Fe, Zn, As, Pb, Ba, Mn, K et Rb) sont associées à diverses sources, lesquelles normalement impactent différenciellement les stations. En effet, on observe des différences entre sites: à La Paz, deux sources potentielles de Fe on été identifiées : l'une serait d'origine naturelle, crustale, et l'autre avec une contribution plus importante, serait liée aux processus de fonderie industrielle. A Las Condes, la combustion de bois est responsable des émissions de K et de Rb, ce qui est un marqueur caractéristique de ce quartier résidentiel.
Par contre, dans les deux stations le Zn et l'As sont associées soit à la combustion de charbon soit aux activités minières.

L'utilisation de la composition en Terres rares (REE), et des rapports La/Ce, La/Sm et La/V permettent d'identifier différentes sources. Nos résultats ont été comparé avec des travaux antérieurs menés à Washington, (Kowalczyk et al., 1982), Philadelphia (Dzubay et al., 1988), Delft (Nederland) (Wang et al., 2000), Houston (Kulkarni et al., 2007) and Mexico (Moreno et al., 2008). A Santiago, les rapports La/Ce et La/Sm dans les PM2.5 permettent le traçage d'une pollution par des catalyseurs utilisés dans les processus de raffinage du pétrole (Fluid Catalytic Crackers ou FCC) et la combustion de pétrole dans les centrales électriques, tandis que le rapport La/V trace la pollution provenant de la combustion d'hydrocarbures riches en FCC. Cette pollution est significative à La Paz tandis qu'à Las Condes le signal est faible.

Les résultats confirment que la station La Paz est plus « impactée » par l'activité industrielle et le trafic automobile que la station Las Condes. Néanmoins, dans des conditions météorologiques spécifiques, la signature de l'activité minière observée à Las Condes est significative.

L'ensemble des résultats démontre une décroissance des concentrations de la plupart des éléments (majeurs et traces), au cours du temps, ce qui confirme l'efficacité des politiques en matière d'amélioration de la qualité de l'air. Néanmoins quelques éléments sont constants au cours du temps et leur origine apparait liée soit à la combustion de pétrole soit à la combustion de bois mais aussi probablement liée aux activités minières (mines, fonderie et raffinerie). En particulier certains éléments – comme l'arsenic - présents dans la fraction PM2.5 conservent de hauts niveaux de pollution qui parfois dépassent les standards établis par l'OMS.

4.3 Geochemical features on urban aerosols in Santiago de Chile from time-series analysis

Valdés Ana, Polvé Mireille, Munoz Marguerite, Toutain Jean-Paul, Morata Diego

First draft of an article to be submitted to…

This explains that some of the informations detailed in chapters 1 and 2 are recalled and summarized here.

Abstract

We analyzed 202 aerosol samples collected in 2004 and 2005 in two sites (one in a commercial-industrial area and one in a residential area) of Santiago (Chile). Fine (PM2.5) and coarse (PM 10) fractions were analyzed by ICP-MS at LMTG, Toulouse, France.

Seasonal gravimetric trends are obvious with higher concentrations in winter for both fractions due to bad conditions of air circulation. Comparison between sites point out systematic higher PM concentrations downtown than in the residential district.

Chemical elements Enrichment Factor (EF) calculation allows to discriminate between lithogenic (EF<10; Mg, Y, Zr, U Sr, Ca, Ti, V) and anthropogenic (EF>10; Rb, K, Cs, Fe, P, Ba, Mn, Ni, Cr, Co, Zn, Sn, Pb, Cu, Mo, Cd, As, Ag, Sb) sources for these elements. Factor analysis applied to major and trace elements concentrations then allows the identification of more specific potential sources of emission of these elements. Three main sources are then proposed: (1) a natural source (crustal - oceanic) to which Al, Ca, Na, Mg, Fe and Ti, Sr, Zr are related; (2) an industrial combustion source, which carries Ni, V, Cr and Fe; and (3) a copper smelter source, characterized by high levels of Cu, Mo, As, Zn and Pb. Moreover, at La Paz we identify two potential sources for Fe: combustion / industrial smelting processes and crustal, meanwhile the presence of Mn could trace unleaded gas combustion. At Las Condes, K appears associated with Rb, which could indicate an origin from wood combustion, consistent with its residential character. In both places Zn appears related with at least two sources, copper smelter and oil/coal combustion.

Among REE, some ratios are efficient tracers of either Fluid Catalytic Crackers (FCC), oil-fired power plants, or catalytic exhaust systems. La/Sm ratios in PM2.5 trace a potential pollution by FCC and/or oil-fired power plant whereas high La/V ratios are compatible with FCC pollution. This pollution is significant in La Paz site, while being nearly negligible in Las Condes. Finally, at both sites, La/Ce ratios lower than the mean crustal ratio can be related to slight contributions of Ce-oxides rich catalytic exhausts.

Comparisons performed between previously published data (1998) and our data set display a clear decreasing trend for most chemical elements, as an effect of the new environmental policies. But some elements do not show this decrease, they are either related to oil/wood combustion, due to restriction on less pollutant fuels, or related to copper industry (mines, smelters, refineries) which has been booming for the last 15 years.

As a conclusion, the study of major and trace elements concentrations, enrichment factor (EF) and factor analysis (FA) has allowed the recognition of the main pollution sources in Santiago and their relative contributions in the two studied sites. The list of chemical elements typical of each source has been confirmed compared to previous studies, and enlarged to some specific trace elements. All indicators, including REE show that La Paz station appears to be more impacted by industrial processes than Las Condes, except when very specific meteorological conditions make the copper smelters source significantly detectable in Las Condes.

This coupled approach shows also the decreasing through time of pollution intensity, for most elements. This confirms the efficiency of the environmental policies adopted by the authorities.

Introduction

Santiago de Chile is a metropolis characterized by a fast urban, industrial and demographic growth (Romero et al., 1999), which results in the increasing exposure of its inhabitants to various forms of atmospheric pollution. Such events are typical of Latin America mega cities (Santiago, Sao Paulo, Mexico City) and result in serious impacts on population health. Due to specific meteorological and topographical features, Santiago displays high levels of pollution fluctuating through most of the year (mean value: 300 µg/m^3 for PM10), with especially high levels (up to 500 µg/m^3) in winter (Jorquera et al., 1998, Artaxo et al., 1999).

Direct relationship between atmospheric pollution and human respiratory - cardiovascular diseases has been established (Ostro, et al., 1996; Ilabaca et al., 1999; Cifuentes et al., 2000; Pino et al., 2004; Roman et al., 2004; Prieto et al., 2007; Cakmak et al., 2007, O'Neill et al., 2008). In particular, increases of children respiratory diseases are reported following main winter pollution events (Ostro et al., 1996). These global health effects have also a significant economic impact (Cifuentes et al., 2005). Despite evident causal relationship, responsible processes are not completely understood and a clear identification of harmful components still lacks in Santiago context. Besides the well known role of gases and organic carbon, only a few studies have been dealing with metallic trace elements concentrations in aerosols (Artaxo et al., 1999; Hedberg et al., 2005), in spite of their suspected role in cardiovascular and respiratory diseases (Ostro et al., 2007; Cakmak et al., 2009; Valdes et al., in appendix A).

Since the early eighties, the Santiago authorities have built a two-levels strategy against increasing pollution: they set up a monitoring atmospheric air network (MACAM) surveying particles and main anthropogenic gases concentrations, and they seriously modified the local policies about toxic emissions through a decontamination program. It induced a severe decrease of major pollutants (PM10, O_3, NOx, SO_2, CO_2) through the removal of fixed sources (diesel generators, waste burning, large wood and coal burning), improvement of the transportation fleet, and introduction of catalytic converters for new cars. Nothing was done, however, against indoor heating kerosene and residential wood burning (Gramsch et al., 2006).

The above-mentioned facts suggest that the anthropogenic emissions to the Santiago atmosphere are evolving continuously. Up to now, only one study on trace elements chemistry of the Santiago aerosols is available (Artaxo et al., 1999).

The main objective of this paper is to propose a detailed geochemical (major and trace elements) characterization of the urban aerosol of Santiago, with a focus on trace metal contents. Two years (2004-2005) sample series of PM10 and PM2.5 were collected at 2 selected sites. The data are discussed in terms of sources of aerosols (natural vs anthropogenic) and sources of contaminants, supported by the mineralogical study performed previously (Morata et al., 2008). Chemical signatures obtained for this data set are also compared with the data previously published on Santiago (Artaxo et al., 1998) and in central Chile (Hedberg et al., 2005) to discuss about temporal changes of the atmospheric contamination over Santiago.

1 Main features of atmospheric metallic pollution in Santiago

Air pollution in Santiago results from a combination of natural and anthropogenic (mobile, stationary and fugitive) sources (Jorquera et al., 2002). Natural sources are mainly re-suspended dust from eroded remote areas and from soils within the city, ocean and biogenic sources (pollens). Other sources are anthropogenic: mobile sources, including on- and off-road transport sources (car, buses, trucks, airports, ports); stationary sources (industrial, commercial and residential sources); and fugitive sources, including agriculture, construction and both paved and unpaved road erosion. Major industrial facilities, including copper smelters and oil refineries, power plants, chemical industries and mining activities (among which the world class El Teniente Mine) are located throughout or close to the metropolitan area of Santiago (Tsapakis et al., 2002) (fig 1). The three copper smelters, Caletones (90 km south of Santiago) and Ventanas and Chagres (150 km north of Santiago) are strong SO_2 and volatile metals (Cu, Zn, As, Pb, Mo) emitters (Romo-Kroger et al., 1994; Hedberg et al., 2005) that affect large areas (Kavouras et al., 2001; Olivares et al., 2008; Gallardo et al., 2002) with a significant impact on agriculture (Garcia-Huidobro et al., 2001).

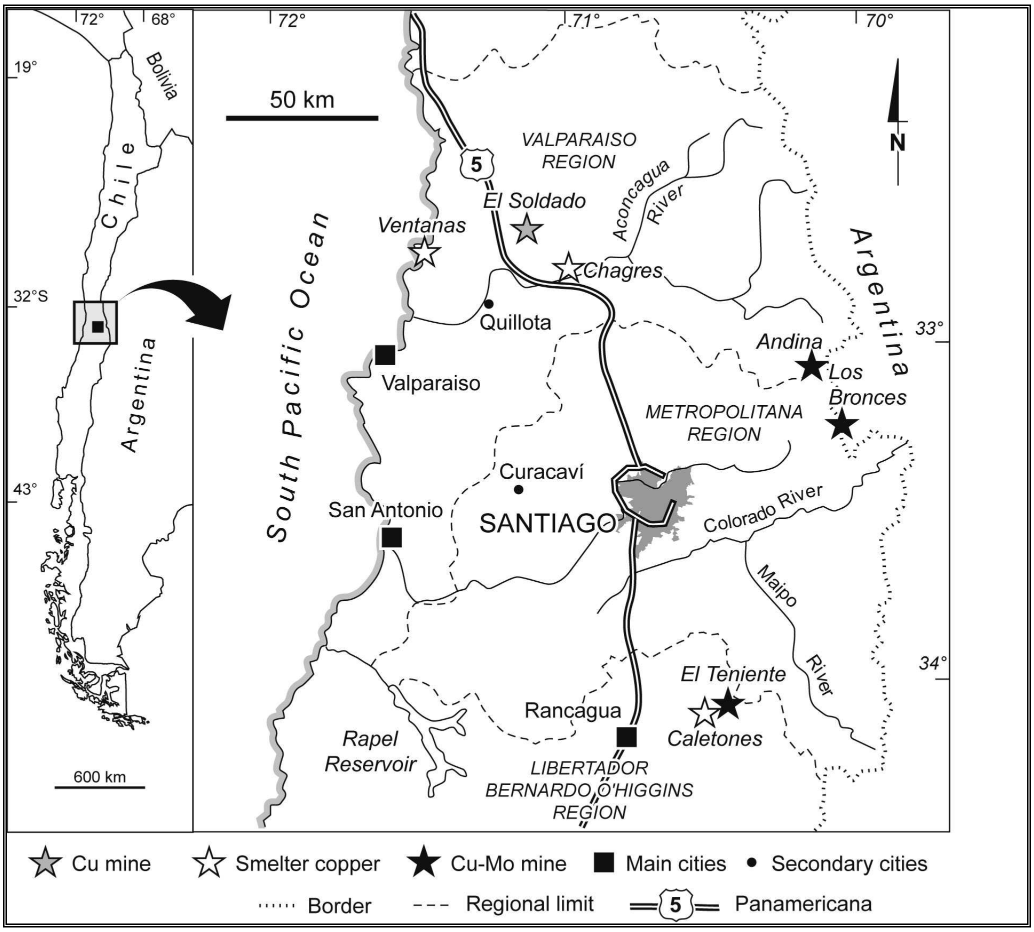

Figure 1: General location of Santiago (from Sernageomin geological map 1:100000; 1999) with mention of the main roads, cities, mines and smelters.

Limited chemical and mineralogical studies of PM10 and PM2.5 allowed to identify the contributing sources to atmospheric pollution in Central Chile (Kavouras et al., 2001; Hedberg et al., 2005) and Santiago (Artaxo et al., 1999; Morata et al., 2008). They evidenced extreme pollution events with total PM10 concentrations reaching 430 µg m^{-3}. The main sources were identified by Factor Analysis (FA) to be mainly soil dust (coarse particles) and traffic emissions (mainly in the fine fraction). Additional minor sources were also identified: residual oil combustion, industrial sources, sulfates from gas-particle conversion, and Cu-smelters (Artaxo et al., 1999). They also pointed out the difficulty to assess precisely the origin of elements, many metals being tracers for several sources. A more recent study performed in the Metropolitan Region (DICTUC, 2007) suggested that the contributions to the particulate matter budget were mainly from stationary source, in decreasing order: industry, firewood burning from residential areas, agriculture burning and residential heating.

The change (nature, flux, chemical features) with time of the contributing sources is likely to induce global changes of particles composition in Santiago. For example, the relative contributions of mobile and stationary sources to PM2.5 budget in the 1990s have increased of 100% and decreased of 50%, respectively (Jorquera et al, 2002). Pb, Br and S patterns have changed following the introduction of new cars equipped with catalytic devices and the growing use of S-depleted diesel. Finally, the continuous evolution of the heating modes in the last decades probably led to continuous changes in the anthropogenic loading of metals in the atmosphere due to indoor heating (Ruiz et al, 2010).

2 Santiago de Chile general context

2.1 Geography and climate

Santiago de Chile (33,5° S, 70.8° W) is a 7 millions inhabitants metropolis which spreads between 450 and 750 m a.s.l within a confined basin located between the Andes Cordillera (> 4500 m a.s.l) and the Coastal Range (< 2000 m a.s.l, fig 1). Yearly rainfall are less than 312 mm (www.meteochile.cl), and temperatures range from -2° C to 35°C with average T° around 10°C in winter and 20°C in summer. High-pressure, anticyclone conditions prevailing in central Chile (between 27°S and 42°S) lead to stable warm and sunny summer to cold and clear winter conditions over Santiago. Most days, an inversion layer prevents both vertical air movements and mixing between air masses, supplying optimal conditions for the accumulation of polluted air (Romero et al., 1999). Regional NE-SW winds are dominant, being much stronger during the day than during the night and allowing the horizontal transport of pollutants within the basin (Rutllant and Garreaud, 1995). Extreme events of air pollution typically occur from April to August, when the inversion layer is as low as 150 m above the ground, with PM10 concentrations reaching 240–300 $\mu g/m^3$ (Adonis and Gil, 2000).

2.2 Geology

Santiago is located in a sedimentary basin filled with Quaternary coarse to fine alluvial sediments derived from the erosion of the Cenozoic volcano-sedimentary formations outcropping in the Andes (fig 2). Three steep hills inside the city are andesitic to dacitic domes or necks covered by the same Quaternary alluvial material. The 450 ± 60 ka old Pudahuel rhyolitic tuff (e.g. Stern 1984) crops out along the western side of the town. Both the alluvia and rhyolitic tuffs are unconsolidated and covered by scarce vegetation, which becomes dry in summer, leaving unprotected soils during a large part of the year. These volcano-sedimentary formations host metallic ores, some of which are or have been exploited, as well as quarries.

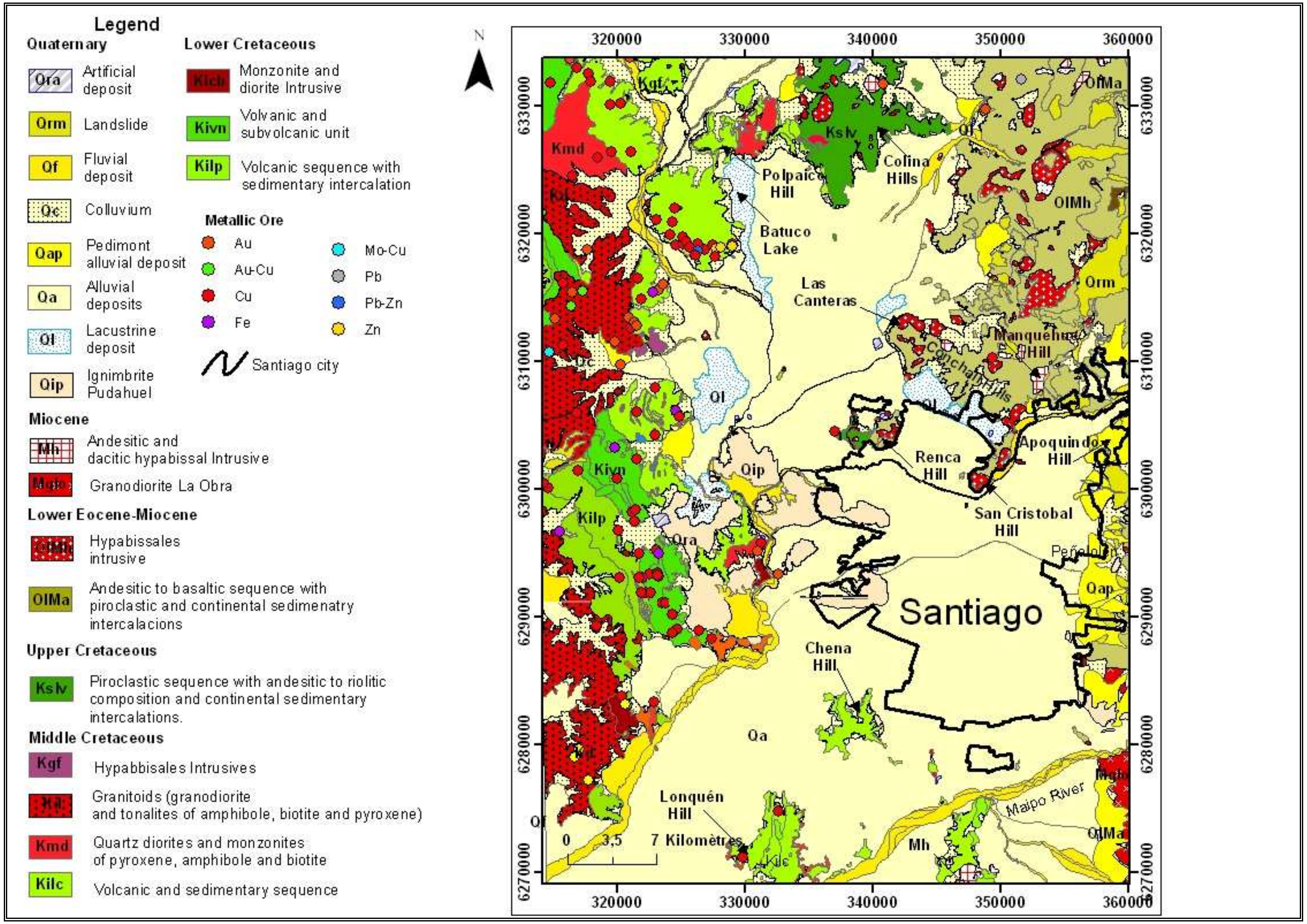

Figure 2: Schematic geological map of the Santiago area (35°) (from geological map of Sernageomin, 1999. 1:100000)

3 Sampling sites and methods

The filters have been supplied by the Monitory Quality of Air Network (MACAM NET, Santiago). MACAM operates 8 stations distributed over the metropolis with automatic and semiautomatic monitoring systems for CO, SO_2, O_3, particles (PM10 and PM2.5), and, for 3 of them, with continuous measurement of NO_3, temperature, humidity, solar irradiation and wind direction. Aerosols investigated here were collected at the 2 sites of La Paz and Las Condes, which are typical of contrasting conditions of Santiago (fig 3). La Paz station (LP) is in the center of Santiago in a mixed (industrial/residential/commercial) district. Its surroundings display four main roads with heavy traffic, a crematory and various boilers, small-size industries and power-supply installations. Las Condes (LC) station is in a residential area partly covered with vegetation. Only a few polluting installations (boilers, heaters, power generators) are located in its surroundings.

Samples were collected with a Dichotomous sampler (Sierra Andersen 244, Smyrna, GA) on 4cm diameter Pall-Flex Teflon filters. This method allows the collection of particle with sizes lower than 2.5 µm (fine fraction: PM2.5) and in the range 2.5–10 µm (coarse fraction: PM10) with a bulk flow rate of 16 – 18 l mn^{-1}. It is worth noting that, because of the filtration system, what is called PM10 here does not corresponds to the generally admitted definition of PM10 i.e. all particles with size under 10µm. This has to be kept in mind when doing comparison with other data. Sampling time is 24 h for all samples. 202 samples from LC and LP stations were selected among the filters collected in 2004-2005 by MACAM (3 to 5 samples per month, representing both the more and the less polluted days of a given month). Filters were weighed before and after sampling with a ± 1µg microbalance, and stored in sterile Petri dishes in dry chambers with controlled humidity and temperature conditions.

4 Analytical techniques

Major and trace elements analyses have been performed at LMTG (University of Toulouse - France) in a class 1000 clean room. Before analysis, filters were cut in 4 sections using cleaned ceramic knife and Teflon tools, in order to keep material for complementary analysis while reducing contamination risks. Filter sections were digested in 7ml Teflon beakers using the following procedure: 100µl of triple-distilled Methanol and 200µl of double-distilled 14N HNO_3 were first added to the sample and left on a hot plate for 12 to 24 hours at 100° C, after being in an ultrasonic bath for 1/4h. 100 µl supraclean 15N HF and 200µl 14N HNO_3 were then added and beakers were left for 48 hours at 150°C. Digestion was usually complete, and the content was evaporated at 50°C. Dry residue was recovered with 50µl 14N HNO_3. In-Re internal standards solution then ultrapure water were added giving 2ml of a 0,37N HNO_3 final solution, ready for ICP-MS analysis.

We used an Agilent 7500 ICP-MS equipped with a collision cell. Elements were analyzed using at least 2 isotopes when possible, with two analytical modes: with or without gas in the collision cell. Indium was used as internal standard and Re as a control of the validity of this standardization. External calibration was done with home-made, non matrix-matched, solutions The protocol applied for internal standard and interference correction was based on Aries et al. (2000).

The 202 analyzed samples correspond to 101 PM2.5 samples from and 101 PM10 samples. We kept for discussion the 48 elements which had at least 80% of measurements above the detection limit (DL = 3x standard error of analytical blanks). They are the major elements (Na, Mg, Al, K, Ca, Fe), trace elements (P, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, Mn, As, Sr, Rb, Zr, Mo, Ag, Cd, Sn, Sb, Ba and Pb, Hf, Ta, W) and rare earth elements (from La to Lu). The mean total blank contribution to elemental contents is about 10% for most elements. It reaches 15 % for Mg, Sc, Co, Sr, Nd, Sm and Th. For 50 to 75% of the samples, the blank contribution is in the range 20-80% for P, Ca, Cr, Ni, Zn, Sb, Hf, W, U, which makes the concentrations of these elements affected by a larger uncertainty.

To validate analysis, we performed 12 duplicates of randomly chosen samples: another fraction of each filter went through the complete analytical process. Table 1 shows the difference between the two analyses, expressed as follows:

$((X-Y)*2/(X+Y))*100$

where X is the concentration of an element in the duplicate and Y is the concentration of this given element in the first analysis. Concentrations of major elements (Na, Al, K, Ca and Fe) differ by 50%, with the exception of Mg which has a better reproducibility (Table 1). Discrepancies between duplicates for metals are much lower, especially in PM2.5 where they are as low as 17% (Zn) and 0% (As, Pb and Mo). Moreover, at both stations, reproducibility is better for fine fractions than for coarse fractions. All these observations are better explained by the greater heterogeneity of coarse particles than by any analytical problem.

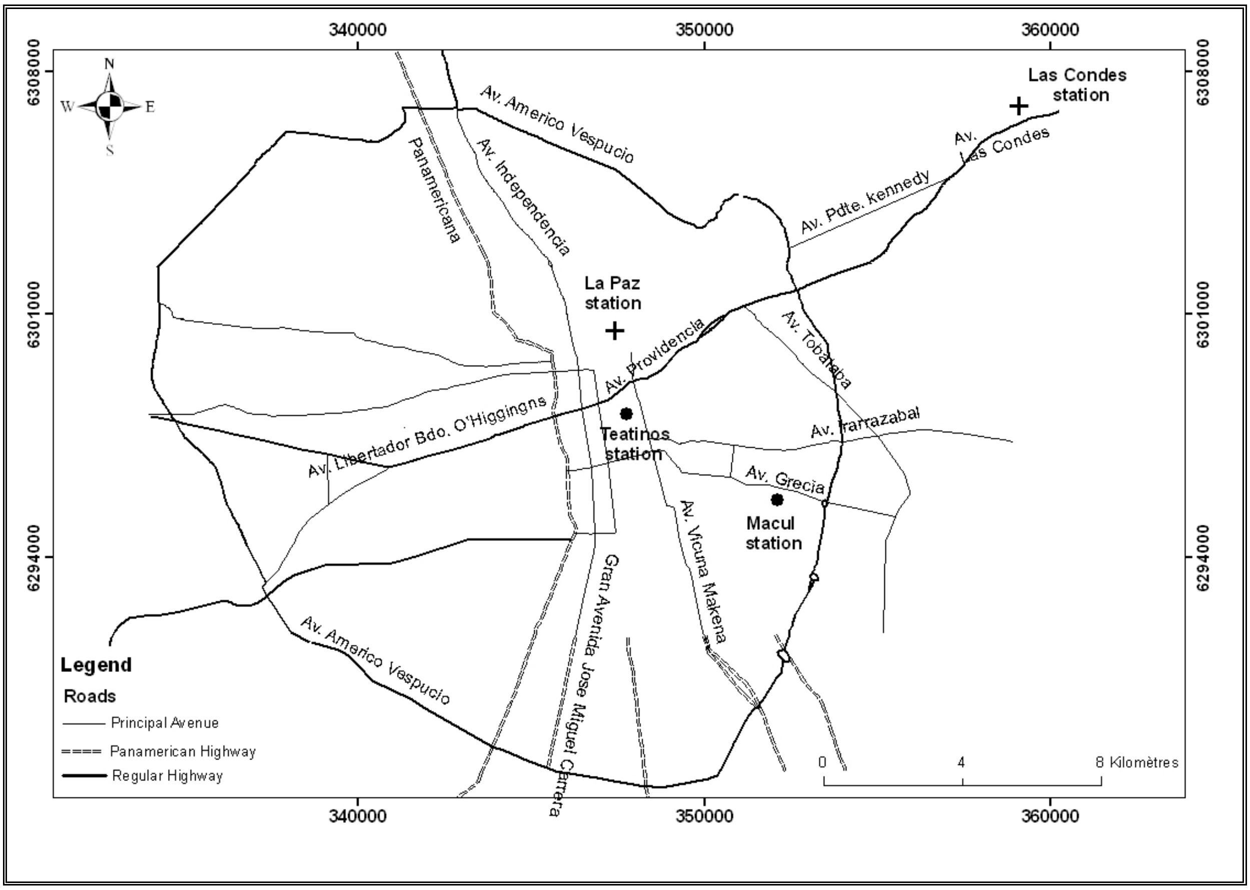

Figure 3: Principal highways and avenues in Santiago, with mention of the four stations studied here (modified from geological map of Sernageomin, 1999. 1:100000).

5 Results and discussion

5.1 PM concentrations in the air

5.1.1 Seasonal variations

Results of the 2 years monitoring of PM 2.5 and PM 10 are displayed on table 2 and 3 and on fig 4 for both stations. A seasonal trend is obvious, as already observed (Gramsch et al., 2006; Artaxo et al., 1999). Higher average concentrations are recorded in winter at both stations, indicating that the main process is linked to global meteorological conditions rather than to local source effects. Indeed the main seasonal effect is probably the drastic reduction of atmospheric turbulences and thinning of the mixing layer in the colder months with the subsequent reduction of pollutants dispersion. On the contrary, high-temperature summer months are characterized by strong vertical turbulences leading to active dispersion. Figure 4 shows that besides the regular seasonal trends, short-period fluctuations can be observed, with abrupt decrease of concentrations. They may be linked to rainfall events that both washout pollutants and decrease the re suspension of coarse particles from ground and soil erosion. Such effect was also already observed by Gramsch et al. (2006).

5.1.2 Variations between sites

Mean values of total breathable particles (PM2.5 + PM10) can be calculated over the 2 years-sampling campaign. They are 90±55 and 66±41 $\mu g\ m^{-3}$ for La Paz and Las Condes stations, respectively (fig 4). Concentrations at La Paz are significantly higher than at Las Condes, in 2005. La Paz is in a central, highly urbanized area which is likely to release pollutants and logically displays the highest concentrations. These average concentrations are close to the ones calculated for the same years by Moreno et al. (2010) in the MACAM station of Parque O'Higgings. Both La Paz and Parque O'Higgins are downtown Santiago, while Las Condes station is in a less densely built residential area. These differences are thus in accord with their respective environments.

5.1.3 Variations through sampling period (2004-2005)

From 2004 to 2005, mean yearly concentrations increase by 5% and 9 % at La Paz and Las Condes, respectively. But the average value found for Las Condes over 2004-2005 is lower than the one reported by Artaxo et al. (1999) during the 1996 period sampling (76.8 $\mu g\ m^{-3}$). If the trend from one year to the next can be due to possible variations of the yearly meteorological conditions (rainfall, winds), the trend over ten years has to be linked to the general decreasing trend observed for PM10 at a nearby station (Parque O'Higgings) between 1996 and 2006, (CENMA, 2009). This trend is largely attributed to the global decrease of the polluting particles input in the atmosphere as the result of major policy inflexions.

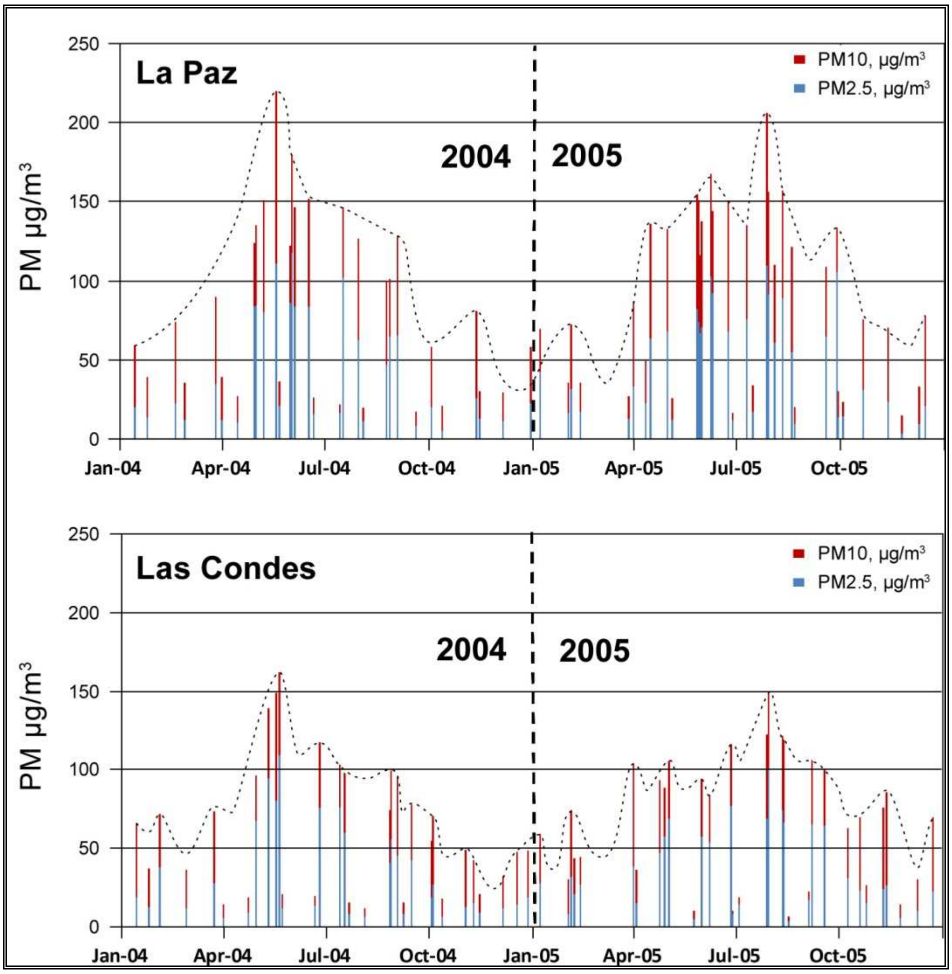

Figure 4: Aerosol mass concentrations for fine (PM2.5) and coarse (PM10) particles. Values are in µg/m^3. This figure shows time series of PM2.5-PM10 at La Paz and Las Condes stations.

5.1.4 Average concentrations compared to international norms

The standard annual average values established by WHO (World Health Organization) are 20 µg/m^3 of PM 10 and 10 µg/m^3 of PM 2.5, while the European Commission proposes 40 µg/m^3 and 25 µg/m^3 as annual averages for coarse and fine fractions. Annual average concentrations for total breathable particles (PM10+PM2.5) and for PM2.5 in Santiago are higher than these recommended values. However, these annual concentrations are lower than those observed in 2002 for the PM 10 in Sao Paulo (~ 149 µg/m^3), Bogota (~220 µg/m^3), Beijing (166 µg/m^3). Peak concentrations in Santiago can reach levels as high as 500 µg/m^3, to compare to the equivalent in Mexico (894 µg/m^3) (Molina et al., 2004).

5.1.5 Comparison between PM10 and PM2.5 concentrations

Time-series of PM 2.5/PM 10 ratios (fig 5) display a clear seasonal trend with ratios higher than 1 (PM2.5 > PM10) in winter (april-september). Trends for bulk concentrations and concentrations ratio are similar, suggesting that the same process controls both variations. Fig 6-a and b display daily series of meteorological parameters (DGAC data in www.meteochile.cl and MACAM network). High levels of concentrations and PM2.5/PM10 ratios are correlated with low wind velocities (fig 6b). This phenomenon is typical of the winters in central Chile (Sandoval et al., 1993; Morales et al., 2006), characterized by weak vertical exchanges within a very thin mixing layer, while a strong thermal inversion layer blocks any upward ventilation.

Interactions between geographic, dynamic and meteorological factors are likely to occur to account for concentrations discrepancies between stations.

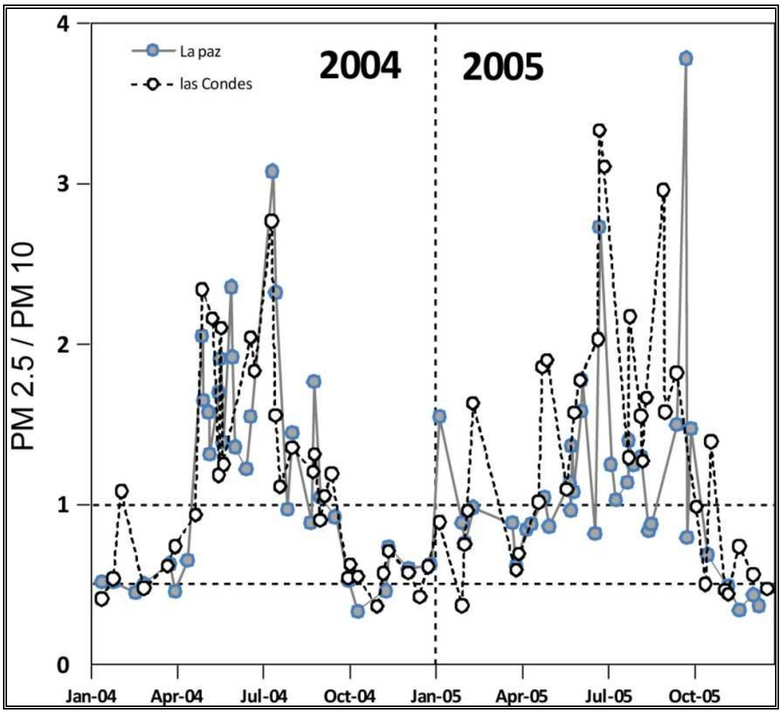

Figure 5: Time series of PM2.5/PM10 ratios.

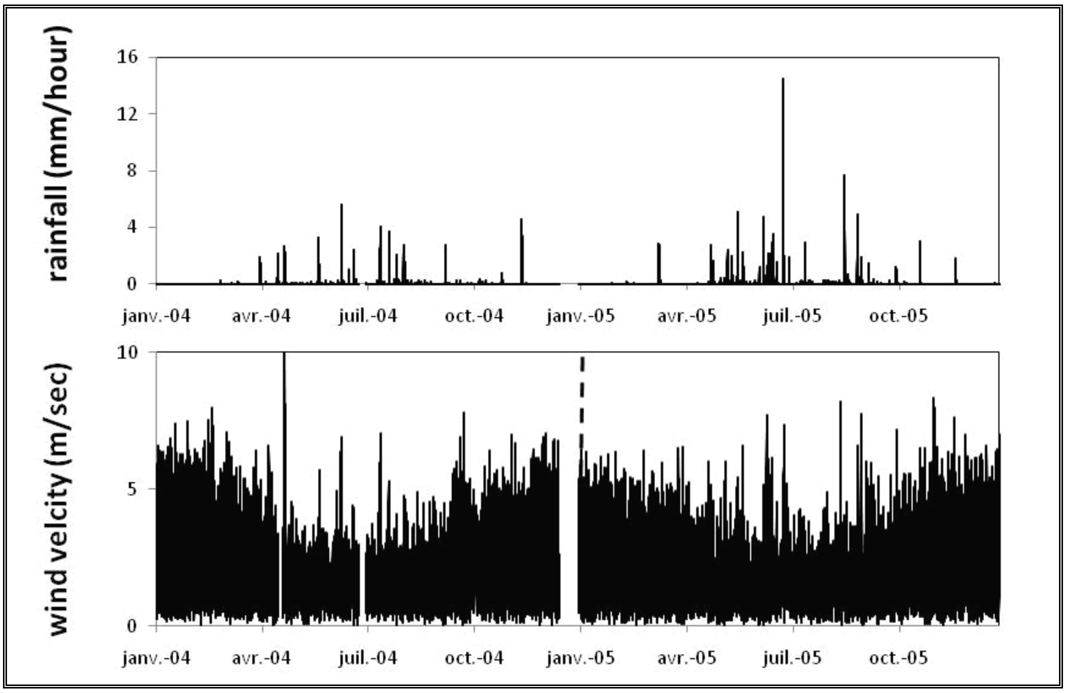

Figure 6: time-series of wind speed and rainfall (hourly values), from La Platina station (South of Santiago). Source: DGAC data (www.meteochile.cl) and MACAM network.

5.2 Sources identification

5.2.1 A methodology used to treat the data in order to discriminate the sources

The urban pollution is a mixing between natural and anthropogenic sources, therefore the identification of each one of them is essential in order to diminish the level of pollution. Three methodologies have been used:

First, enrichment factor in order to discriminate between natural and anthropogenic origin of the elements analyzed. This methodology corresponds to the ratios of analyzed elements which we will discuss in detail in 5.2.2 section.

In the second step the factor analysis has been used to identify the elemental association that corresponds to specific sources. Through Factor Analysis (FA) and Principal Components Analysis (PCA) (table 5), we used the concentrations of the above-mentioned elements in order to identify underlying variables, or factors, that explain the pattern of correlations within our set of observed variables (Reimann et al., 2008). The values (loading) in the matrix represent the associations between each variable and each of the one retained factors. The results allow the recognition of three principal factors which explained 85% of total variance in La Paz and 89% in Las Condes. Each factor has been interpreted as one source using the elements with loading ≥ 0.6. Associated to each main source, we recognized minor contribution, which are identified using elements with loading between 0.5 and 0.6. That is consistent with a complex urban pollution, which mixes regional and local emissions, controlled by meteorological processes (wind speed and directions). The principals results obtained from here we will discuss in 5.2.3.

Finally based on the proportion of some Rare Earth Elements (La/Sm, La/Ce, La/V) the identification of modern industrial processes as a refinery of petrol is possible. We will explain this point in detail in 5.2.4.5 section.

5.2.2 Natural versus anthropogenic source discrimination

All chemical analyses are given in tables 4 (a, b, c, d, e, f, g, h). It is nearly impossible to comment on this huge amount of data and distinguish trends and tendencies. Thus data will be treated statistically. They will be first discussed through the concept of Enrichment Factor.

Here, Enrichment factors (EF) aim to emphasize the influence of the two main sources (anthropogenic *vs* lithogenic). EF are calculated with respect to a lithogenic element (typically Al, Zr or Th), and allow to show the respective level of enrichment of all elements compared to the mean crust composition. EF are calculated as follows:

$EF_x = (C_x/C_{ref})_{sample} / (C_x/C_{ref})_{crust}$

where $(C_x/C_{ref})_{sample}$ is the ratio of concentration of an element x to the reference element in the sample and $(C_x/C_{ref})_{crust}$ is the same ratio in the typical crustal material.

We used here the bulk mean crust as defined by Taylor and Mc Lennan, (1995). Al has been chosen here as reference element because it is usually assumed to have no anthropogenic source (Calvo et al., 2008) and to be resistant to most surface processes. EF higher than 1 is typical of a contribution of sources other than crustal, but a threshold of 10 is considered to be more reliable to discriminate between crustal and non-crustal origin for the elements (Parehk et al., 1989; Morata et al., 2008).

The elements Mg, Y, Zr, U Sr, Ca, Ti, V display systematically EF<10 for both fractions and both sites in 2004 as well as 2005 (fig 7). These elements are typical lithogenic elements. One must note than their EF are systematically higher for PM2.5 than for PM10 at La Paz station, whereas their enrichment level is similar between fractions at Las Condes. This may suggest that different processes act in the two sites, with primary lithogenic particles impacting in Las

Condes area whereas finer lithogenic particles are collected at La Paz station, probably through the selective remobilization of sedimented lithogenic particles.

Another class of elements (Rb, K, Cs, Fe, P, Ba, Mn, Ni, Cr, Co, Zn) show medium EF (in the ranges 10-10^3 and 10-10^2 for PM2.5 and PM10, respectively). Finally, the highly enriched elements (Sn, Pb, Cu, Mo, Cd, As, Ag, Sb) have EF between 10^3to10^6 in the PM2.5 fraction.

Fig 7 shows that the higher the EF, the higher the discrepancy between enrichment levels in PM10 and PM2.5. This is clear at both stations for all elements except Sb. This suggests that anthropogenic contaminants are released mainly as fine particles, probably through high-temperature processes as they favor small size particles as shown by Morata et al. (2008) from SEM observations.

On the contrary, Sb shows the highest enrichment level and, at the same time, displays only slightly more enriched signature in PM2.5 than in PM10. Sb might come from two different anthropogenic sources: the first one, related to erosion processes of ore deposits would provide coarse particles while the other, related to industrial processes would provide fine ones.

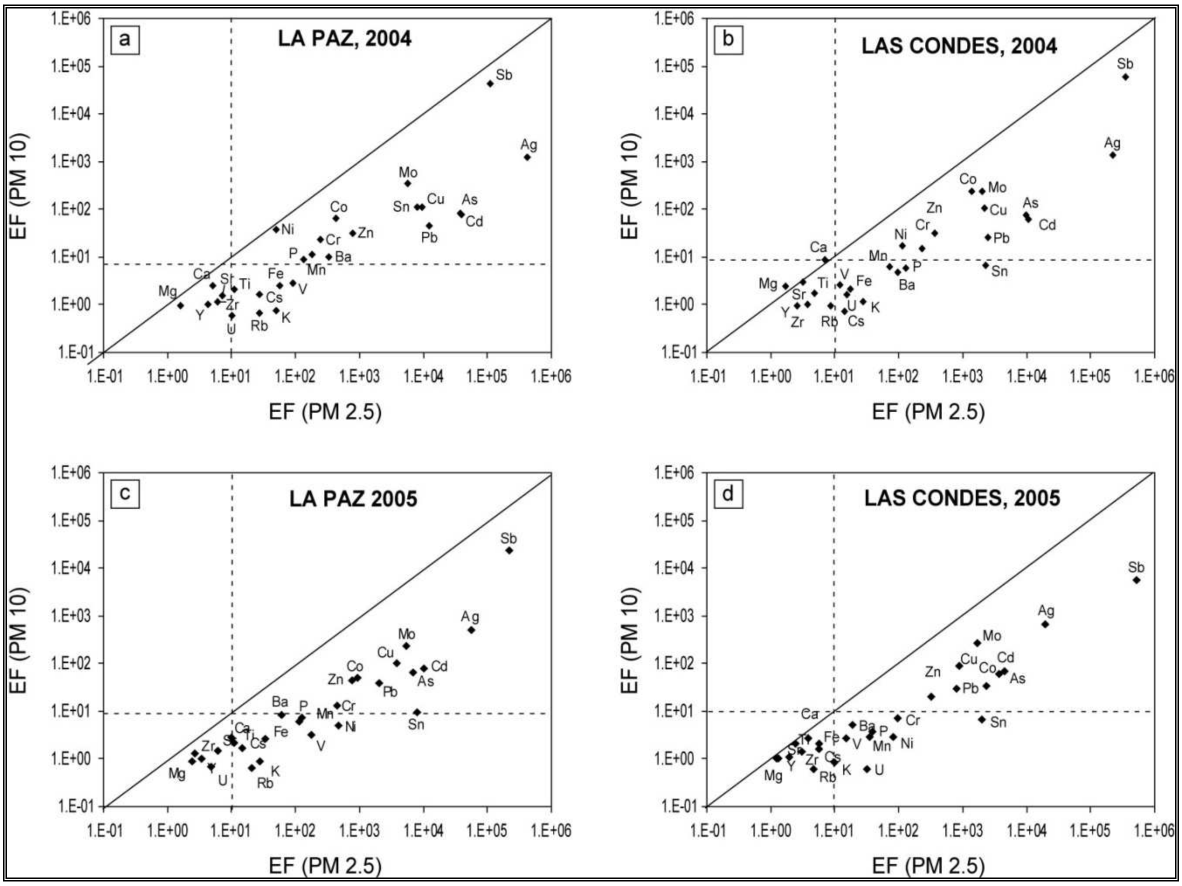

Figure 7: Enrichment factors for PM2.5 and PM10 at both sites. Reference element is Al. The enrichment factor is calculated with respect to the mean crust (Taylor and Mc Lennan, 1995). a,c: La Paz 2004,2005. b,d: Las Condes 2004,2005.

5.2.3. Natural Source

Factor Analysis on the PM2.5 fractions at both stations, allow to recognized two sources with a natural origin:

At la Paz, the **first factor** displays high loadings (≥ 0.6) (table 5) for the major elements Al, Ca, K, Mg, Mo, Na, and the trace elements Rb, Sr, V, Ti, Zr, and loading between 0.5 ≤ to < 0.6 for Ba, Cr, Fe and Zn. The major elements Al, Ca, Fe, K, Na and Mg and some trace elements such as Ti, Sr and Mn are used as tracers of natural origin (Artaxo et al., 1999, Morata et al., 2008, Moreno et al., 2010, Kavouras et al., 2001). Na and Mg are classically associated with salts of marine origin (Hedberg et al., 2005, Kang et al., 2009). But we can add the elements Zr and Rb which also display high loadings in this first factor and can be considered then as tracers of natural source.

5.2.3.1 Lithogenic Source

The major elements Al, Ca, Fe, K, Mg, Na, and trace elements such as Ti, Sr, Mn, Zr and Rb have a crustal origin within Santiago, as shown both by EF and FA-CPA analysis. This feature can be interpreted as the signature of a *crust-related source* (phyllosilicates, feldspar, pyroxene and amphibole, iron oxides) (table 5) and is in agreement with Morata et al. (2008) on two others sampling sites in Santiago.

This confirms the works of Artaxo et al. (1999), Moreno et al. (2010) in Santiago (table 6) and Romo-Kröger et al. (1994), Kavouras et al. (2001) and Hedberg et al. (2005) in nearby towns (table 7). Both tables regroup the major sources identified as either regional or local, natural or anthropogenic of particles in the air of Santiago from PM10 and PM2.5 fractions and corresponds to a set of chemical elements defined by previous authors regrouped table n° 6 (for Santiago) and n° 7 (for other towns in Central Chile). In these tables, elements which were used in FA-PCA and are common to most authors are underlined, elements in black have been considered by each author as typical of a given source, while elements in grey are secondary elements mentioned by the authors. Sources will be considered now under their type, local or regional and the signature we characterized for them will be compared to the elemental associations determined by other authors.

Beside this set of elements, we associated Ba, Cr, Fe, Mo, V and Zn to this crust-related signature, while Artaxo et al. (1999) and Moreno et al. (2010) do not associate these later elements but recognize a crust-related origin for Mn. Hedberg et al. (2005) add Si to this list of crustal elements, actually this seems obvious, as the major part of the upper crust is made of silicates. In addition to the typical crust-derived elements, in the coarse fraction from Viña del Mar, Br, As, Cu, Zn and Pb also appear to be crust- related (Kavouras et al., 2001), while only Mn and Ba are thought to have a crustal origin in Valparaiso. Some of these elements (Mn, Pb and P) were also associated to the crustal source defined within the fine fraction by Artaxo et al. (1999) in Santiago. We will see frequently this problem, when comparing chemical signatures of the other sources. Indeed, many elements are related to more than one source, and then one author will affect the element to one of these sources while others will affect it to another source. We will not discuss in details these variations and consider that the first mentioned set of elements is soundly demonstrated as tracing the lithogenic source in Santiago area.

5.2.3.2 Marine Source

This natural source can carry a *marine* contribution, traced here by Na and Mg that present the highest loading (0.91) in factor 1 (table 5). This marine source has been suggested by Hedberg et al. (2005) in Quillota and Linares, two towns closer to the ocean than Santiago (table 7).

We associate the elements Mg and Na to marine sources following Moreno et al. (2010) who argue that Na, Cl and Mg may be related to marine aerosols, carried by westerly winds to the Santiago basin (table 6). The work of Hedberg et al. (2005) supports this conclusion, but without Cl analyses in our data set, we cannot discuss this point any further. Mg is a constitutional element in some minerals such as pyroxene and amphibole (Morata et al., 2008), so probably another origin for Mg is related to crustal sources, however according to Hedberg et al., 2005 and Moreno et al., 2010 Na and Mg have been used to trace marine aerosols. Indeed the positive correlation (~0.80) between Mg and Na in both fractions obtained using the Pearson matrix, allows this hypothesis to be supported.

In factor one, a minor contribution mixed with the crustal source could be suspected from Ba, Cr, Fe, Mo, V and Zn (table 5). Although Ni is not in this list as it presents a smaller loading (0.38), we propose to consider it with V, as tracers of oil combustion, while Cr is associated with coal combustion in agreement with Hedberg et al. (2005). Mo and Zn are confirmed to be related with copper industry, which is indeed not surprizing as they are present in Cu ores **(**Romo-Kroger et al., 1994). Ba, which belongs to this minor mixed contribution, could be present as $BaSO_4$ as proposed by Morata et al. (2008). The origin of this sulfate stays unclear at it could be both natural (gypsum) of anthropogenic (plaster).

5.2.4 Anthropogenic Source

Seven anthropogenic sources were identified at Santiago. Five of them correspond to a set of chemical elements defined by previous authors (table 6 and 7). In this way, the elements as Cu, Zn, As, Mo, Pb, Bi and Ag are currently used as tracers of copper smelter (Hedberg et al., 2005, Romo-Kroger et al., 1994, Kavouras et al., 2001). V and Ni are widely associated with oil combustion (Celis et al., 2004; Pey et al., 2009) and less frequently Zn appears related also to this source (Artaxo et al, 1999 and Moreno et al., 2010). The elemental association Sb, Pb, As, Zn and Co is associated with coal combustion (Moreno et al., 2007) and Cr also has been related to this source by Hedberg et al., 2005. K is considered as a tracer of wood combustion together with Rb (Carvacho et al., 2004, Celis et al., 2006).

On the other hand, two additionally sources (processes of refinery of petroleum industry and the power plant) were traced using rare earth element.

5.2.4.1 Copper smelters

The **second factor** displays elements with loadings ≥ 0.6 for Ag, As, Ba, Bi, Cd, Cu, Fe, Mo and Pb, and minor associated loadings ($0.5 \leq$ loadings < 0.6) for Rb, V, Ti (table 5). This signature fits with copper smelters being the principal source (Kavouras, et al., 2001; Batonneau et al., 2004; Morata et al., 2008) with minor lithogenic and oil combustion contribution.

The elements used as tracers were: Cu, Zn, As, Mo, Pb, Bi and Ag and the new elements associated to this source in Santiago are: Zn, Pb, Bi, Ag, Ba, Cd, Fe, Mn.

According to our results, the association of elements (Cu, Zn, As, Mo, and Pb), is confirmed as tracer of copper smelters. This list of elements associated to copper smelters is regional (table 7), as it has also been recognized in Viña del Mar, Valparaiso, Quillota and Linares (Kavouras et al., 2001, Hedberg et al., 2005). The association of S to copper smelters has been demonstrated by several authors (Romo-Kroger et al., 1994, Hedberg et al., 2005) and S should be added to this signature, but we have not measured S concentrations and cannot discuss it. Ag, Bi are also associated to this factor, in agreement with Hedberg et al. (2005) who relate Cu, Mo, As and to a lesser degree, Ag, Bi, Zn, Pb to smelter sources at Quillota and Linares. Actually, Hedberg et al., 2005 and us, are ending with the same list of elements. We only differ or their relative importance. We both agree on Cu, Mo and As as major ones to which we add Zn and Pb. As minor elements we both found Ag and Bi.

We also got Fe, Ba, Cd and Mn as first order elements associated to copper smelter source. This is no surprising as these elements are either present in the copper ores or involved in the refining processes. SEM studies can provide complementary arguments in order to discriminate between particles from copper ores and particles generated in copper smelters. The first ones will have irregular or in the best cases, crystal shapes. On the contrary, the morphological and chemical composition of particles studied by SEM (Morata et al., 2008 and non published data) reveal the occurrence of spherical particles, around 1 um diameter, bearing usually some metal (Fe, Zn, Cu). The origin of such anthropogenic particles is related to high temperature processes.

5.2.4.2 Coal /Oil combustion

In the **third factor** (table 5)**,** Co, Cr, Mn, Ni and Sb display loadings ≥ 0.6 and Zn in the range 0.5-0.6. This corresponds to coal combustion source as defined by Moreno et al. (2006 and 2007) with minor loading for As (0.21) and Pb (0.25). The presence of Ni could trace a oil combustion minor contribution, but as V does not appears with a significant loading in this third factor, the oil combustion source is not soundly demonstrated.

All authors agree that the association V - Ni traces oil combustion (table 6 and 7). Through our study, we propose to add Sb, Pb, As, Zn, Cr and Co as tracers of this source. This association has already been found as representative of coal combustion in Spain (Moreno et al., 2007). And, we propose to add REE-V as specific and discriminant tracers of different oil combustion processes (Fluid Catalytic Crackers and oil-fires power plants) (see 5.2.4.5).

It is worthy to note that Pb, As, and to a lesser extent Zn, which are known to be dangerous for human health, appear linked to this source.

5.2.4.3 Traffic

In La Paz station (table 5), the presence of Mn in the third factor, could trace combustion of unleaded gas with Mn-bearing organic compound (methylcyclopentadienyl-Tricarbonyl-manganese) as anti-explosive (SESMA, 2002 in Celis et al., 2004).

From our study, traffic is from 2004 till now traced mainly by Mn, which is used, as said earlier, as anti-explosive in the unleaded gasoline. All other authors argued that traffic was traced by the Br-Pb association. This is understandable for data collected before 2001, date of the final ban on leaded gas. Moreno et al. (2010) observed the end of this Pb signature in October 2004, while we do not in samples collected in 2004 and 2005. Moreover, we propose REE as tracers for catalytic exhaust pipes (thus traffic) pollution.

5.2.4.4 Biomass/wood burning

Similar results are obtained at <u>Las Condes station</u> (table 5), with some difference in the intensity of some sources, except for K (associated with Rb) which has been considered as a local source, because it is characteristic of this neighbourhood. K and Rb display here a significant loading (> 0.5) in the second factor. This may be related to wood burning, quite frequently used for residential heating (Kovauras et al., 2001; Hedberg et al., 2005). We thus propose to add Rb in association to K currently used as tracer of wood combustion in Santiago (table 6). This association is supported by Kavouras et al. (2001) in Rancagua, Viña del Mar and Valparaiso. The association between Zn and K is probably related to wood burning (Hedberg et al., 2005) (table 7).

In both stations we confirm that Fe can be provided by two potential sources: an anthropogenic one, related with combustion or industrial smelting processes (as demonstrated through our FA analysis) and a natural lithogenic one, as already observed by Morata et al. (2008). But when looking in more details, in La Paz, Fe appears more strongly associated with others metals such as Cr, Mo, Zn, than with elements of clear lithogenic origin (Al, Ca, K, etc). Therefore we suggest that Fe, in La Paz, is mostly anthropogenic and more specifically related with copper smelters or metallurgic process. On the contrary in Las Condes, the two sources, natural and anthropogenic are detectable and coexist.

In both places Zn also appears related with more than one source, copper smelter and oil/coal combustion.

Treatments applied to PM10 data do not discriminate groups which could be related with clear origins whatever the site. At both stations, only 2 principal factors are identified and the differentiation between sources is not obvious. Most elements are concentrated in the first factor, while Co, Cr, Ni, Zn, Bi and Sb are mainly displayed in the second factor. Based on Moreno et al., (2007), Sb, Pb, As, Zn and Co are associated with coal source (table 8). Therefore, even if the loadings of Pb and As are fairly low (0.4), the presence of Sb at Las Condes in association with Zn and Co, might be related to coal combustion. In fact, the presence of Cr confirms this observation (Hedberg et al., 2005). The second elemental association (As, Ba, Bi, Cd, Cu, Mo, Pb) with loading between 0.4 to 0.5 suggest cooper smelting contribution observed in the second factor at Las Condes. This signal is not clear in La Paz. In addition, Sb contribution it not observed in the PM10 fraction of La Paz station.

Finally the prescence of Zn in two factor with loadings (0.5 to 0.7) in both stations, suggest more than one source for Zn: copper smelter and oil/coal combustion process.

Mn is only present at La Paz and could indicate a combustion of unleaded gas with organic manganese compound.

Loadings:	La Paz			Las Condes		
	Factor 1	**Factor 2**	**Factor 3**	**Factor 1**	**Factor 2**	**Factor 3**
Principal contribution	**Natural Source crustal/sea**	**Cu Smelter**	**Combustion process (coal/oil)**	**Cu Smelter/ Crustal**	**Natural Source crustal/sea**	**Combustion process (coal/oil)**
Minor contribution	oil/coal combustion; copper smelter	crustal origin; oil combustion		oil/coal combustion;	burning of biomass; oil combustion	
Ag	0.32	0.72	0.10	0.68	0.58	
Al	0.89	0.26	0.22	0.55	0.70	0.17
As	0.18	0.88	0.21	0.86	0.20	0.31
Ba	0.52	0.76	0.18	0.87	0.38	0.23
Bi	0.30	0.83	0.35	0.89	0.29	0.27
Ca	0.82		0.42	0.21	0.85	0.25
Cd	0.34	0.84	0.30	0.90	0.21	0.30
Co			0.88			0.95
Cr	0.51	0.49	0.62	0.53	0.36	0.70
Cu	0.44	0.83	0.26	0.88	0.39	0.25
Fe	0.58	0.78		0.85	0.45	0.21
K	0.76	0.39	0.27	0.70	0.60	0.15
Mg	0.94	0.18	0.25	0.38	0.87	0.20
Mn	0.37	0.35	0.67	0.87	0.36	0.26
Mo	0.64	0.61	0.13	0.82	0.36	0.20
Na	0.91		0.19	0.34	0.91	
Ni	0.38	0.42	0.73	0.45	0.26	0.76
Pb	0.32	0.88	0.13	0.90	0.25	0.25
Rb	0.71	0.55	0.19	0.78	0.56	0.11
Sb	0.14	0.21	0.89	0.19		0.94
Sr	0.81	0.19	0.48	0.57	0.78	0.17
V	0.70	0.56	0.15	0.76	0.51	
Zn	0.55	0.36	0.54	0.52	0.40	0.63
Ti	0.76	0.58		0.68	0.59	0.19
Zr	0.74	0.48	0.14	0.74	0.57	0.11

Table 5: Main sources identified at Santiago from Factor Analysis (FA) in PM2.5 fraction. Values represent loading obtained from FA. Loadings ≥ 0.6 correspond to natural sources (e.g. crustal/marine origin), copper smelting and combustion processes. Loadings < 0.6 correspond to a minor contribution.

Source / **Author and year of sampling**	**Natural Sources**		**Combustion**		**Transport/ automobil emissions**	**Sulfate/ secondary sulfate**	**Copper emissions**	**Biomass/ Wood burning**
	Dust	**Sea**	**Oil**	**Coal**				
Valdes [1] 2004, 2005	**$PM_{2,5}$**: **Al, Ca**, Fe, **K, Rb, Sr, V, Ti, Zr**. Ba, Cr, Mo, Zn.	**$PM_{2,5}$**: **Mg, Na.**	**$PM_{2,5}$**: **V**, **Ni**.	**$PM_{10-2,5}$-$PM_{2,5}$**: Sb, Pb, As, Zn and Co; Cr	**$PM_{2,5}$**: Mn; REE.		**$PM_{2,5}$**: **Cu**, Zn, **As, Mo, Pb, Bi, Ag, Ba, Cd, Fe, K, Mn.** Al, Cr, Rb, Sr, V,Ti, Zr.	**$PM_{2,5}$**: **K.**
Artaxo (1996)[2]	**$PM_{2,5}$**: **Al, Ca, Fe, Si, Ti, Sr, Mn** (Pb, As, P).		**$PM_{2,5}$** : **V, Ni, S, Zn, Cl, Mn**.		**$PM_{2,5}$**: **Br, Pb, Cl,** K and Sn.	**$PM_{2,5}$**: **S, Se, K, P.**	**$PM_{2,5}$**: **S, Cu, As, Mo, K, P.**	**$PM_{2,5}$**: Zn, Cu.
Moreno[3] (1998-2007)	**$PM_{10-2,5}$-$PM_{2,5}$**: **Al, Ca, Si, Ti**. **$PM_{10-2,5}$** : **Fe, Mn, Mg, Sr.**	**$PM_{2,5}$**: Na, Cl. **$PM_{10-2,5}$**: Na, Cl, (Mg).	**$PM_{10-2,5}$-$PM_{2,5}$**: **Mn, Cu, Fe, Zn,** Pb. **$PM_{10-2,5}$**: **Ba, Cr.**		**$PM_{2,5}$**: **Br, Pb**,Cl, K, (~S).	**$PM_{2,5}$**: **S, P.**	~S	
Morata[4] (2004)	**$PM_{10-PM2,5}$**: **PIXE: Al, Ca, Fe, Si.**				**SEM**: FeO.	**PIXE**: S S-K/Ca S- (Fe,Mn, Cr,Ti). **SEM:** $CaCO_3$, $CaSO_4$, $BaSO_4$.	S	

Notes: [1]Valdes et al., (in preparation); [2]Artaxo et al., 1999; [3]Moreno et al., 2010 and [4]Morata et al, 2008.

Table 6: Chemical signatures are compared for Santiago. Sources are identified as either regional or local, natural or anthropogenic. Elements that are common to all authors are underlined; elements in bold have been considered by some author as typical of a given source, while the elements in grey represent secondary elements mentioned by the authors.

Source **Author and year of sampling**	Natural Source		Combustion		**Transport/ automobil emissions/ motor vehicle**	**Sulfate/ secondary sulfate**	**Copper emissions**	**Iron or steel Industry**	**Wood/ agricultural burnings**	**Diesel emissions (Truck or ship) and Local refinery**
	Soil dust	**Sea salt**	**Oil**	**Coal**						
Romo-Kröger[1] 1991 (Caletones-La Leonera)	**fine-coarse fraction**: Al, **Ca**, **Fe**, **Si**, **K**, Ti.						**fine-coarse fraction:** **S, Cu, Zn, As.**		**fine-coarse fraction:** **K, Ca, S.**	
Kavouras[2] (1998) (Rancagua)	**$PM_{10-2,5}$ - $PM_{2,5}$:** **Al, Ca, Fe, Si, K, Ti, Sr, Mg.**				**$PM_{10-2,5}$ $PM_{2,5}$**: **Br, Pb** (K, V, Fe, Ni, As, Cu, Mo and Zn).		**$PM_{10-2,5}$ - $PM_{2,5}$** : **S, Cu, Zn, As, Mo.**	**$PM_{10-2,5}$-$PM_{2,5}$**: **Ti, Cr, Mn, Fe, Zn, Zr, Mo.**	**$PM_{10-2,5}$-$PM_{2,5}$:** **K**, Ca, Fe, Rb, Br.	
Kavouras[2] 1998 (Viña del Mar)	**$PM_{10-2,5}$ - $PM_{2,5}$:** **Al, Ca, Fe, Si, Ti** and only for **$PM_{10-2,5}$** : Br, As, Cu, Zn, Pb, K.	**$PM_{10-2,5}$**: Cl.	**$PM_{10-2,5}$ - $PM_{2,5}$:** ~S.		**$PM_{10-2,5}$ - $PM_{2,5}$**: **Br, Pb.**	**$PM_{10-2,5}$ -$PM_{2,5}$:** **S** (Cu, As, Zn,Pb,V,Ni).	**$PM_{10-2,5}$-$PM_{2,5}$:** **Cu, Zn, As, Mo, Pb.**		**$PM_{10-2,5}$ -$PM_{2,5}$:** **K**, Fe, Rb, Sr.	**$PM_{10-2,5}$-$PM_{2,5}$** **V, Ni,**~S.
Kavouras[2] 1998 (Valparaiso)	**$PM_{10-2,5}$ - $PM_{2,5}$**: **Al, Si, Ca, Fe, Ti, Mn, Ba.**	**$PM_{10-2,5}$**: Cl.	**$PM_{10-2,5}$ - $PM_{2,5}$:** ~S.		**$PM_{10-2,5}$-PM_{10}:** **Br, Pb** (K, Ca, Sr and Ba)	**$PM_{10-2,5}$ - $PM_{2,5}$:** **S, As.**	**$PM_{10-2,5}$ - $PM_{2,5}$**: **Cu, Zn**, As, **Mo**, Pb.		**$PM_{10-2,5}$-$PM_{2,5}$** : **K** , Ca, Br, Rb.	**$PM_{10-2,5}$-$PM_{2,5}$**: **V, Ni**/~S
Hedberg[3] 1999-2000 (Quillota, Linares)	**PM_{10}**: **Al, Ca, Fe**, Si, **Ti and Mn.**	**PM_{10}**: **Mg, Na**, Br, (Ni, V,Cr,**S**).	**PM_{10}:** **Ni, V.**	Cr.	**PM_{10}**: **Br, Pb,**V, N		**PM_{10}:** **Cu, Zn, As, Mo**, Bi, **Ag.**		**PM_{10}**: **K** and **Zn** (Rb).	

Notes: [1]Romo-Kröger et al., 1994; [2]Kavouras et al., 2001; [3]Hedberg, et al., 2005.

Table 7: Chemical signatures are compared for Central Chile. As in table 7, sources are identified as either regional or local, natural or anthropogenic, and elements that are common to all authors are underlined; elements in bold are mentioned only by some author as typical of a given source, while the elements in grey represent secondary elements mentioned by the authors.

Station	La Paz		Station	Las Condes	
Source / Elements	Mixing of Crustal, Cu smelter, oil/coal	oil/coal/industry combustion	Source / Elements	Mixing of crustal, Cu smelter, oil/coal	oil/coal/industry combustion
Ag	0,43		Ag	0,42	
Al	0,91		Al	0,95	
As	0,88		As	0,81	0,42
Ba	0,92		Ba	0,87	0,44
Bi	0,81	0,53	Bi	0,79	0,52
Ca	0,90		Ca	0,92	
Cd	0,89	0,40	Cd	0,83	0,47
Co		0,95	Co		0,90
Cr	0,71	0,61	Cr	0,56	0,77
Cu	0,92		Cu	0,87	0,44
Fe	0,92		Fe	0,93	
K	0,87	0,46	K	0,91	
Mg	0,93		Mg	0,96	
Mn	0,46	0,86	Mn	0,93	
Mo	0,85		Mo	0,79	0,44
Na	0,79	0,48	Na	0,89	
Ni	0,52	0,80	Ni	0,47	0,80
Pb	0,92		Pb	0,84	0,47
Rb	0,88	0,41	Rb	0,95	
Sb	0,97		Sb		0,95
Sr	0,86	0,49	Sr	0,94	
V	0,90	0,41	V	0,93	
Zn	0,55	0,66	Zn	0,49	0,73
Zr	0,87		Zr	0,89	0,41

Table 8: Main sources identified at Santiago from Factor Analysis (FA) in PM10 fraction. Values represent loading obtained from FA. Loadings ≥ 0.6 correspond to natural sources (e.g. crustal/marine origin), copper smelting and combustion processes. Loadings < 0.6 correspond to a minor contribution.

5.2.4.5 Industrial processes contributions from Rare Earth Elements signatures in Santiago aerosols (and crustal values of references)

Rare earth elements (REE) are new comers in environmental geochemistry as they are more and more involved in sophisticated industrial processes. Indeed, Kowalczyk et al. (1982) made the observation of anomalous La enrichment and high La/Sm ratios in urban aerosols. These authors could not think of any explanation but predicted that when understood, this property will make REEs potential tracers of specific anthropogenic sources.

High La/Sm ratios were later attributed to fluid catalytic crackers (FCC) in refineries and Kitto et al. (1992) provided the basic data on zeolite cracking catalysts used in petroleum refineries in the US, Europe and Japan. They demonstrated that these zeolites display significant Light REE (LREE) enrichment compared to the heavy ones (HREE) with La/Sm reaching values as high as 300. These enrichments were also observed in the volatile part of refined oils. They pointed out that oil-fired power plant also have LREE enrichment (mostly La), but without associated V enrichment. The two sources could thus be distinguished. A new REE pollution has been pointed out as LREE (mostly Ce Oxydes) are used in the catalytic exhausts filters set on the more recent cars, the signature of which is less well constraint but can be suspected nevertheless.

REE data in solid aerosols have been published for the towns of Washington, (Kowalczyk et al., 1982), Philadelphia (Dzubay et al., 1988), Delft (Nederland) (Wang et al., 2000), Houston (Kulkarni et al., 2007) and Mexico (Moreno et al., 2008). All these data will be used for comparison in the interpretation of our own data, together with the general features of each pollution source and the natural (upper crust) REE ratios.

REE concentrations in all PM10 and PM2.5 fractions from the two sites are given in tables 4 and 5. Total REE concentrations reach a maximum of 1.8 and 1.2 ng/m^3 in PM2.5 and PM10 respectively in La Paz and 5.7 and 4 ng/m^3 in PM2.5 and PM10 respectively in Las Condes. These maximum are lower to equal than those observed in Mexico by Moreno et al. (2008) (10 ng/m^3). In Washington and Delft concentrations are also around 10 ng/m^3. Concentration observed at Philadelphia is approximately 50 ng/m^3 while Houston reaches 90 ng/m^3.

5.2.4.5.1 Catalytic Converters

In figure 8 La/Sm ratios are plotted vs La/Ce, both for PM10 and PM2.5 fractions, in Las Condes (fig 8a) and in La Paz (fig 8b). In both sites, La/Sm ratios from PM10 are roughly constant around 5 while La/Ce vary from 0.28 to 0.55 and from 0.22 to 0.52 in Las Condes and La Paz respectively. In other words, La/Sm ratios stay close to a typical “crustal” value, while La/Ce ratios display the same scatter from the crustal value (0.5) in the two sites.

On the contrary, in the two sites, both La/Sm and La/Ce from PM2.5 fractions are scattered. La/Ce are more scattered than in PM10, from 0.23 to 1.56 and from 0.28 to 1.3 in Las Condes and La Paz respectively. La/Sm ratios vary from 5 to 85 and from 5 to 65 in Las Condes and La Paz respectively. La enrichment is partly responsible for this feature, accompanied by some Ce enrichment.

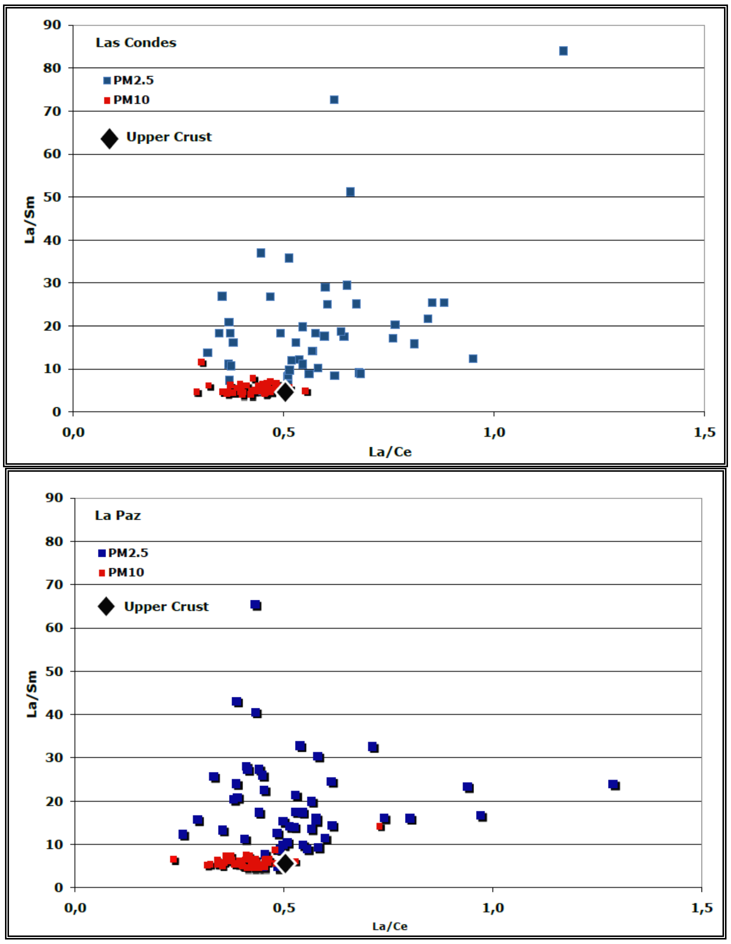

Figure 8: La/Sm ratios are plotted vs La/Ce, both for PM10 and PM2.5 fractions, in Las Condes (fig 8a) and in La Paz (fig 8b).

5.2.4.5.2 FCC and/or Oil Fired Power Plant

In order to better decipher the origin of these La (and Ce) enrichments, La/V ratios are plotted versus La/Ce in figure 9. Strikingly the larger scatter and the higher values are observed in the PM10 fraction. Indeed La/V varies between 0.11 (crustal value) and 0.2 in

PM10 from Las Condes and between 0.5 and 10 in some PM10 fractions from La Paz. On the contrary, La/V in the PM2.5 fractions varies from 0.04 to 0.4 in Las Condes and from 0.05 to 0.2 in La Paz. When checked against time (not shown), ratios far from upper crust values are always found in filters collected during winter times, when pollution reaches its maximum.

La/Sm in PM2.5 fractions display a signature tracing a potential pollution by FCC and/or oil-fired Power Plant. The high La/V values measured are compatible with FCC pollution, but it is quite surprising that these high La/V are found in the PM10 fractions while the high La/Sm are carried by the PM2.5 fraction. Anyhow, this pollution is significant in La Paz while it is nearly negligible in Las Condes. One of the principal thermoelectric plants in Santiago region, which uses diesel and/or natural gas, is located 3,5 km westward of the La Paz station and could account for the high La/Sm. But we have no record of any FCC close to this station.

Finally, at both sites, La/Ce variations towards values lower than the crustal value can be related to slight contribution of Ce-oxides rich catalytic exhausts.

Our data are plotted in figure 10 together with those from other towns. It shows that REE pollution in Santiago is quite moderate compared to US towns specially Houston, surrounded by petrochemical industries and oil refineries. The observation that REE pollution is sometimes more visible in PM10 than in PM2.5 has also been made in Mexico by Moreno et al. (2008) and still needs to be understood.

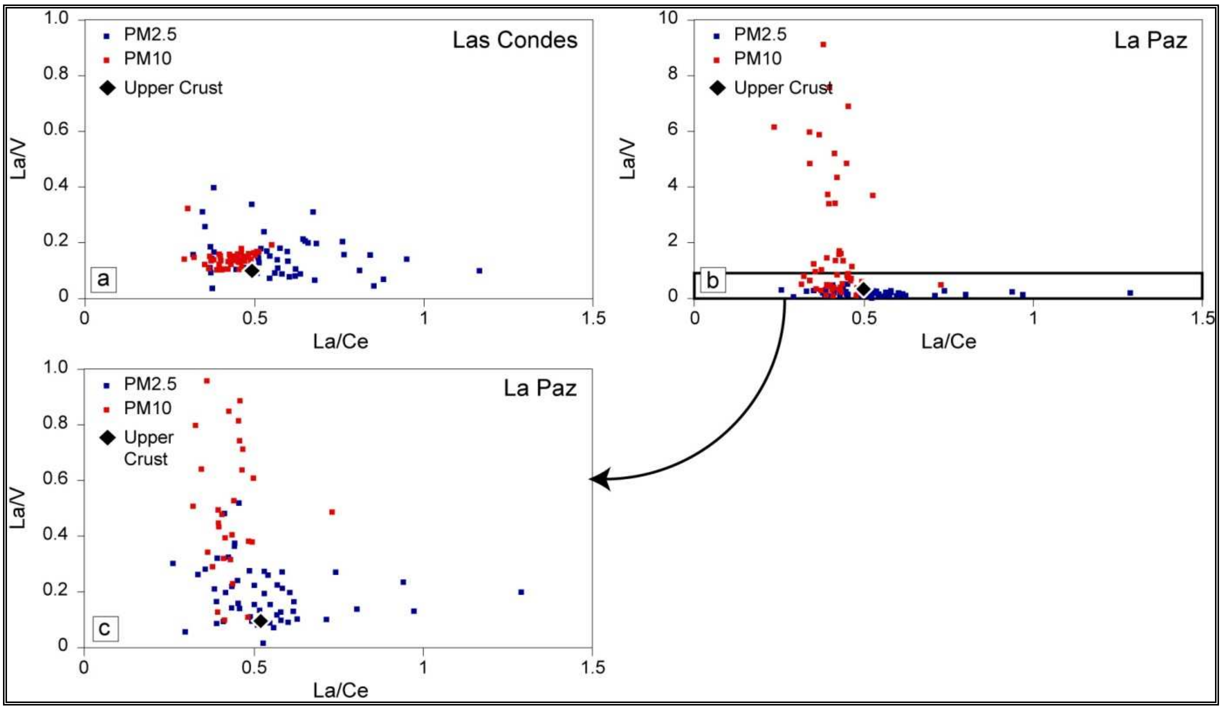

Figure 9: La/V ratios are plotted versus La/Ce. a: in Las Condes, b : in La Paz, c : in La Paz, close up on data with La/V < 1 (as in Las Condes).

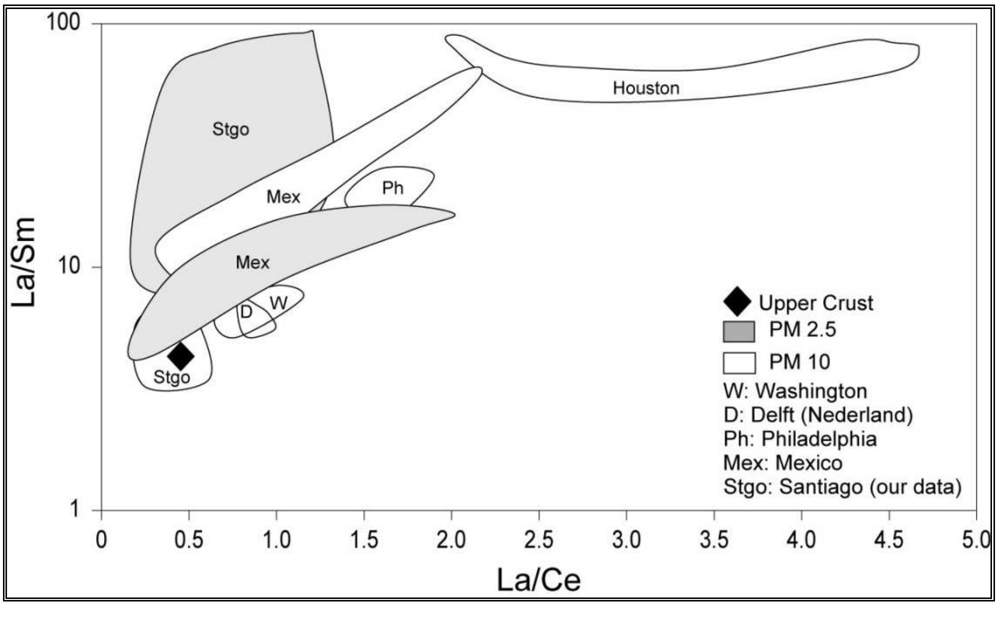

Figure 10: Comparison of REE pollution in Santiago and data from other towns. A quite moderate contamination with respect to US towns (especially Houston) is observed.

5.3 Meteorological consequences on intensity and style of the pollution

We observed that the most polluted days in Santiago were always associated to specific meteorological conditions. Indeed Rutllant (1994) distinguished two major pollution episode types, the H episodes (high pressure), responsible for 70% of the highly polluted days and the BPF episodes (Before Pre-Frontal), responsible for 30%). Both systems are associated with low wind speeds, low altitude thermal inversion and very thin mixing layer over the ground, that is very unfavorable meteorological conditions for pollutants dispersion. BFP systems are associated with clouds and no wind, while H systems present clear skies and sunny days.

We found 8 daily sampled in 2004 and 6 in 2005 in our database, which corresponds to these highly polluted days with specific meteorological conditions. They decomposed in 4 type H episodes, 6 type BPF and 4 of mixed H-BPF.

The highest concentrations ever found, in both sites, are strikingly always associated with the mixed BPF-H meteorological conditions (for example: 27 May, 2004). Therefore it seems that this combination of meteorological systems degrades mechanisms of dispersion and consequently increases the accumulation of pollutants in Santiago. Then, the discriminant parameter seems to be the wind direction which vary during the transition between one system (H) to the other (BPF). Usually this transition is facilitated by westerly winds which transports aerosols from the ocean to the continent and may be responsible for the increase in Na and Mg concentrations, as observed between May 18 and 19, 2004 in La Paz, (Na: 55.79 ng/m^3 to 77.20 ng/m^3).

We also notice that these specific meteorological conditions correspond to a clear “copper smelters” signature (Fe, Cu, Mo, As, Ba and Pb) in Las Condes in both fractions. This shows the regional impact of the different mines and copper smelters – refineries, on the eastern region of Santiago during wintertime. It is also in agreement with the general wind direction (north) observed during cold periods (fig 11). This wind transports aerosols from the copper smelters (Ventanas and Chagres) or Cu mine located ~130 kilometers north of Santiago in the Coastal Mountains (El Soldado, 600 metres a.s.l) or Cu-Mo mines (Andina and Los Bronces, ~4000 metres a.s.l.) located 65 and 100 kilometers to north of Santiago respectively, within the Andes (fig 1). This pollution in Las Condes was higher than in La Paz, in opposition with data on means and average.

Indeed, the close examination of specific highly polluted days, led us to discover that these days displayed features in opposition with what we observed when working statistically on mean values. This is an important remark and it means that the statistic study is not sufficient and may lead to biased conclusions. It has to be completed by daily observations, especially on the highly polluted days. And here is the link with the medical studies as these highly polluted days are the ones sending many people to the hospitals.

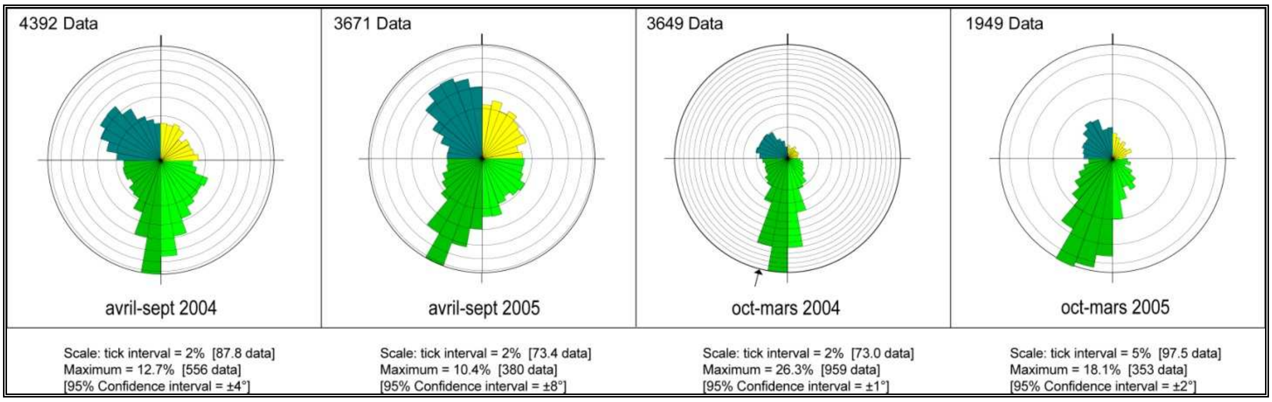

Figure 11: Frequency wind roses between cold (April to September) and warm (October to Mars) seasons in 2004 and 2005. Diagrams for the cold seasons rest on 4392 data in 2004 and 3671 in 2005. For the warm seasons they rest on 3649 data in 2004 and 1494 in 2005. Each interval (tick) corresponds to 2%. The maximum values are indicated in each diagram. This data set was taken from DGAC data (www.meteochile.cl) and MACAM network.

5.4 Evolution of elemental concentrations between 1998 and 2005

In the same way as the comparison we made earlier in this study, based on total PM or PM2.5 concentrations measured two times over 8 years, comparison between elemental concentrations obtained on the same stations and their evolution through time can be made, even if used analytical techniques and sensibilities are different.

5.4.1 Evolution at Las Condes station between 1998 and 2005

5.4.1.1 PM10

All major and trace element concentrations decrease in Las Condes between 1998 (Artaxo, 1998) and 2004/2005 (our study) (fig 12a and b). Al, K and Fe decrease by 75%, Mg, by 55% and Ca by 44%. All trace elements decrease by more than 70%, with the exception of Ni that displays constant values of ~3ng/m^3. This is in agreement with the general decrease of PM10 concentrations observed earlier and has to be related first to the efficiency of environmental policies, even if, from one year to the next, differences in concentration could also be due to changes in meteorological factors such as precipitation. For example, mean monthly precipitation between July and August, 1998 was ~0.5 mm while in 2004 and 2005 it was ~ 80 mm.

5.4.1.2 PM2.5

In Las Condes, PM2.5 fractions, (fig 12 c and d) concentrations in most elements decrease between 1998 and 2004-2005. The decrease observed in Al traces a general decrease of the amount of particles with lithogenic origin, probably due to development of paved roads at the expenses of dirt roads, but here also the high level of precipitation in 2004 and 2005 may have reinforced this feature. In opposition to this general feature, Ca, Fe and K concentrations increase, decoupled from Al. This has to be related to human activity, even if these elements also have a crustal origin. Ca can be linked to $CaCO_3$ quarries and plaster used for construction (Morata et al., 2008), Fe to steel industry and K to wood burning, but we have no explaination for its combined decrease in PM10 and increase in PM2.5.

Sc, V and As concentrations decrease by 70% and Pb by ~65% while Mn and Cu concentrations increase by 40% over these 7 years. Cr and Zn concentrations remain almost constant (with a great variability for Cr). Decreases in V and As are probably due to the industrial atmospheric emission reduction plans. The decrease in Pb may be attributed to the introduction of unleaded gasoline. In spite of these emission policies the increase in Cu and Mn concentrations, combined with constant concentrations of Cr and Zn, show the impact of copper smelting and combustion sources on Santiago.

One can argue that element concentrations, being calculated as averages, could also trace the effect of the total number of highly polluted days (in relation with specific meteorological conditions) within a year. Indeed 16 high pollution days occurred during July, 1998, while during the same month in 2004 and 2005 they were only 4 and 2 days respectively. August 1998 had 6 high pollution days but zero in August 2004 and 2005. Only more frequent geochemical analysis could allow us to argue that the environmental policies are inducing a general and constant decrease of most pollutant concentrations, even if the constant decrease of total PM and PM2.5 concentrations are in favor of this hypothesis.

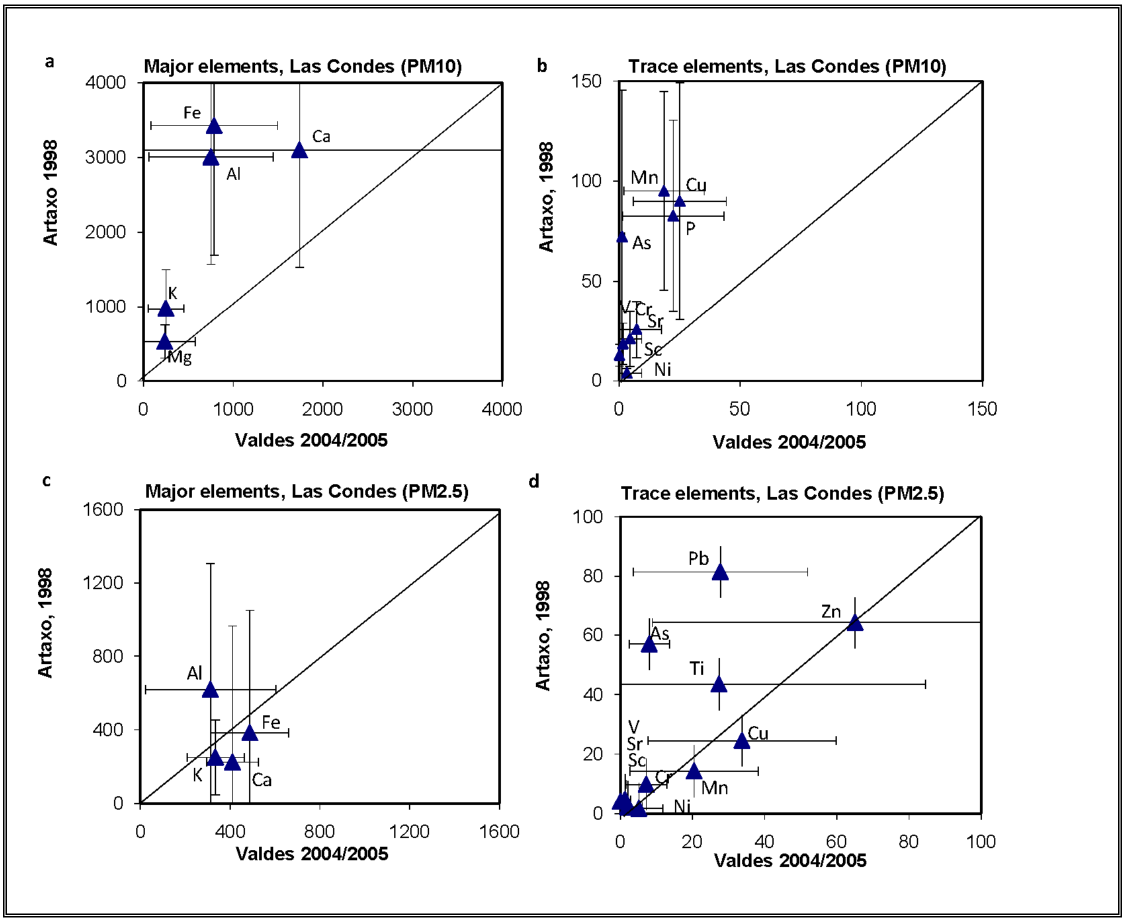

Figure 12: Comparison between 1998 (Artaxo et al 1998) and 2004/2005 (Valdes et al, 2011 (in preparation)) at Las Condes. Some important variations in elemental concentration has been observed in coarse (graphic a and b) and in fine fraction (graphic c and d).

5.4.2 Evolution at La Paz-Parque O'Higgings station between 1998 and 2005

A comparison has been made between data obtained in 1998 in Parque O'Higgings (PIXE data, Artaxo, 1998) and in 2004/2005 in La Paz (fig 13 a and b). Both stations are downtown Santiago, though the La Paz site is slightly more industrial and densely populated than Parque O'Higgings.

5.4.2.1 PM10

Patterns observed in coarse fraction at the La Paz station are similar than those observed at Parque O'Higgings. Major and trace elements decrease over 60% and 50%, respectively. However Ni is almost constant between 1998 and 2004/2005. Therefore, the decrease observed here can be attributed to the same factors as exposed earlier.

5.4.2.2 PM2.5

Tendencies in the fine fractions are identical (fig 13 c and d): a decrease in Mg (43%) and Al (60%) concentrations over time, and an increase around 45% for Ca and Fe concentrations, while K is almost constant.

Ti and Sr suffer a 50% decrease and Sc, V, As and Pb concentrations are reduced by 75%, as observed in PM 2.5 from Las Condes. Again, the increase in Mn (60%), Cu (25%) and Zn (17%) also presents a pattern similar to Las Condes. Cr and Ni present constant concentrations as observed in the fine and coarse fractions from Las Condes.

Ni and Cr are related to oil and coal combustion respectively, and their release in the atmosphere could be due to restrictions on imported gas since 2004, that was replaced by the more polluting diesel and by LPG (liquid petroleum gas) fuel sources. These observations are consistent with FA-CPA analysis.

As a summary, a general elemental concentrations decrease was observed in coarse and fine fractions between 1998 and 2004/2005 in both stations, in agreement with the decrease noted for PM10 and PM2.5 concentrations. We interpret this as a positive result of the environmental policies.

However, some elements escape to this general improvement. Ca concentrations increase is probably related to limestone quarries and plaster industry (Morata et al., 2008) which grew together with the development of the city and the boom in building industry (Moreno et al., 2010). Fe concentrations increase is linked to expanding steel industry, while, as already mentioned, increase in K concentrations is due to the constant use of wood burning in residential areas. The increase in some trace elements such as Cu, Mn and Zn could be related to the copper smelter emissions that are booming over time due to worldwide increased demand for Cu. An overall increase in oil and coal combustion, could explain the constant concentrations in Ni and Cr./

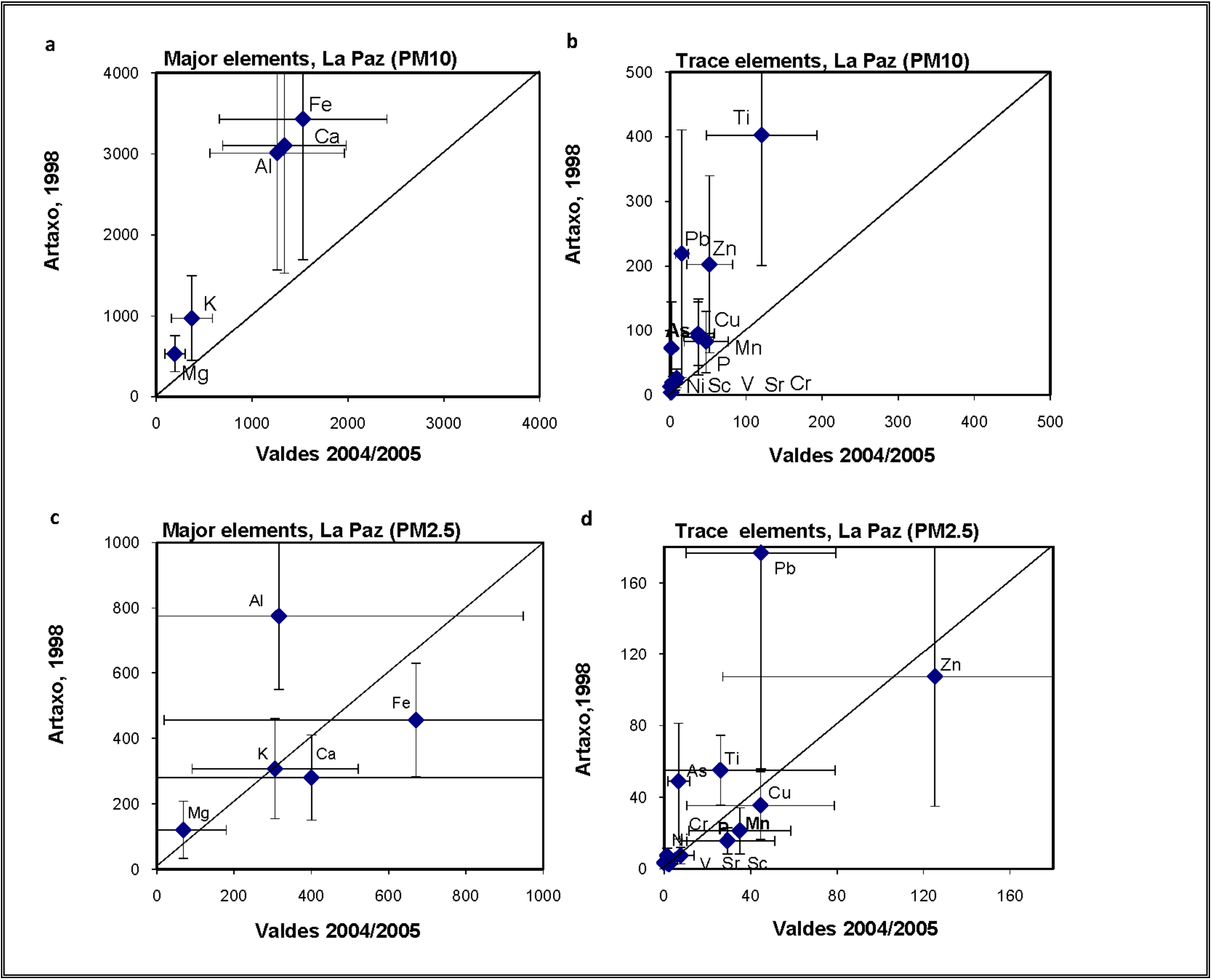

Figure 13: Comparison between 1998 (Artaxo et al 1998) and 2004/2005 (Valdes et al, 2011 (in preparation)) at La Paz and Parque O'Higgigins stations. Some important variations in elemental concentration has been observed in coarse (graphic a and b) and in fine fraction (graphic c and d) .

6 Conclusion

Both natural and anthropogenic sources impacting the city have been identified, sometimes with more elements than in previous studies, due to our extensive analytical program. These new elements such as the REE might be quite useful in further studies. Indeed, as REE are more and more used in industrial processes and in catalytic exhausts, this pollution might increase in the next decades and should be controlled regularly. These preliminary data could be useful then as reference values in any future work in Santiago. Moreover, traffic source cannot be traced as previously by lead due to the ban on leaded gas, thus REE ratios will become precious tracers of traffic through catalytic exhaust pipes REE signature.

Within the local sources, K (wood burning) was observed in eastern Santiago (Las Condes) but does not present any real danger for the inhabitants. On the contrary, Fe presents two possible origins in Santiago aerosols especially downtown (La Paz); crustal origin and industrial processes (smelter copper). Indeed, according with observations on SEM (see 3.4, chapter 3) we also can suggest an origin related with industrial processes at high temperatures such as metallurgic industry.

The comparison between 1996 (Artaxo et al., 1998) and 2004 and 2005 shows a general decrease of PM and most elemental concentrations, in both sites. But, we point out an increase in Cu, Mo and Mn concentrations during the last years of this follow up. Therefore, even if public policies implemented during the observed 10 years have been effective at reducing elemental concentrations, it seems necessary to improve the control on specific elements (identification, reduction), even if their annual average concentrations in PM10 (i.e. As, Pb, Cd, Mn and Ni) are below the accepted standards determined by WHO and the European Community (fig 14). In fact, the As concentrations observed in PM2.5 are three times over the standard levels during specific meteorological configurations (H-BPF and BPF) in days of maximal pollution.

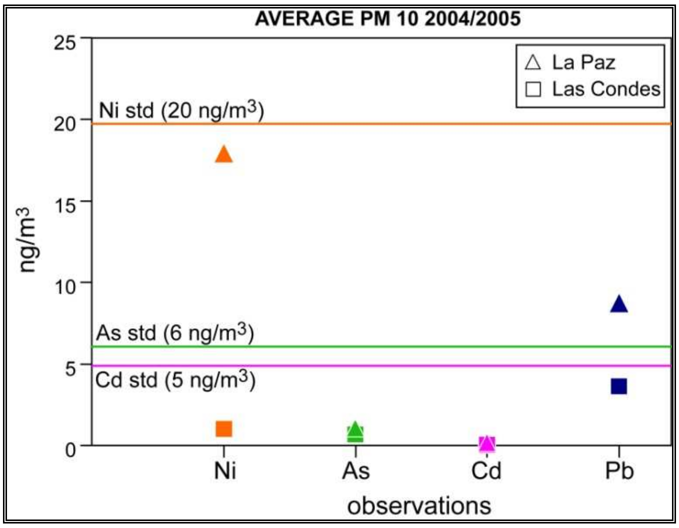

Figure14: Acceptable concentration levels for Pb, Ni, As and Cd are indicated by horizontal lines (as defined by the WHO) and plotted against observations (points) taken from PM2.5 and PM10. Note that the concentration level for Pb (150µg/m^3) is not plotted due to the chosen vertical scale.

Among the sources having regional impact, components of copper production (mine, smelter and refinery) have been recognized in Santiago, impacting sometimes more significantly eastern Santiago (Las Condes). This is the first time that this pollution is clearly detected in Santiago atmosphere, as it had been detected till now only in towns closer to the copper industry sites. Moreover, the list of elements associated to this source has been augmented. For example, the association of Zn, Cu, Pb, Mn to copper smelting in Santiago will help to understand, then could be used, through new policies, to decrease: (1) risk of mortality due to Cu and Zn emissions (Cakmak, et al., 2009); (2) risk of respiratory mortality due to Cl and Zn emissions and (3) chronic obstructive pulmonary disease due to Ni emission (Valdes et al., in preparation, appendix A).

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Percentage duplicates PM10																				
Date	Sample	**Na**	**Mg**	**Al**	**P**	**K**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**
8/23/04	F3-1128	2.02	10.82	24.61	31.63	3.91	14.47	23.71	8.48	12.63	19.87	26.50	24.87	4.51	38.77	21.17	37.57	5.93	4.20	7.43
6/27/05	F3-0754	30.94	22.10	14.77	23.96	25.39	23.59	6.24	7.47	11.85	65.68	8.01	2.47	41.33	196.33	5.04	56.22	5.96	4.67	13.44
7/9/05	F3-0824	37.47	112.50	70.65	14.35	26.93	66.27	70.44	20.09	19.86	130.55	20.98	18.10	11.04	3.32	15.18	4.21	22.77	14.70	1.71
6/20/04	M3-0742	18.27	11.49	23.62	7.49	33.32	55.68	63.63	30.51	33.12	67.38	24.67	18.81	66.90	92.40	24.63	40.77	26.52	29.56	46.72
6/27/205	M3-0758	70.99	9.47	4.05	0.49	27.60	93.25	40.85	8.34	40.04	151.67	0.58	2.08	44.14	0.02	10.46	135.18	0.25	47.91	1.72
7/2/05	M3-0788	39.62	5.32	14.34	17.56	44.26	57.20	0.18	20.45	16.03	2.25	14.64	10.49	102.25	2.89	14.73	73.25	22.12	42.83	14.25
N samples : 0-10 %		1	2	1	2	1	0	2	3	0	1	2	2	1	3	1	1	3	2	3
N samples 10-20 %		1	2	2	2	0	1	0	0	4	1	1	3	1	0	3	0	0	1	2
N samples < 20 %		**2**	**4**	**3**	**4**	**1**	**1**	**2**	**3**	**4**	**2**	**3**	**5**	**2**	**3**	**4**	**1**	**3**	**3**	**5**
N samples % total < 20%		33	67	50	67	17	17	33	50	67	33	50	83	33	50	67	17	50	50	83

Percentage duplicates PM 10																
Date	Sample	**Rb**	**Sr**	**Y**	**Zr**	**Mo**	**Ag**	**Cd**	**Sn**	**Sb**	**Cs**	**Ba**	**Pb**	**Bi**	**Th**	**U**
8/23/04	F3-1128	8.63	17.34	20.58	2.31	74.25	35.60	70.44	44.18	85.15	16.53	35.64	13.91	29.26	40.11	14.13
6/27/05	F3-0754	4.31	4.85	61.09	74.52	20.59	2.80	0.46	29.96	196.29	1.71	12.54	12.96	12.00	55.64	77.50
7/9/05	F3-0824	36.01	30.81	63.62	29.73	14.08	24.97	14.42	2.26	20.10	45.99	26.11	5.00	2.69	59.10	4.85
6/20/04	M3-0742	2.27	18.67	18.91	31.74	32.87	86.72	32.14	74.56	0.20	16.12	25.29	15.02	14.24	58.99	12.42
6/27/05	M3-0758	12.74	16.76	3.82	23.73	12.35	67.77	10.46	5.71	195.63	13.61	11.10	60.05	7.77	105.74	131.72
7/2/05	M3-0788	0.51	4.00	0.64	25.67	10.26	53.25	8.51	9.21	53.70	0.32	0.31	5.58	5.90	86.77	75.14
N samples : 0-10 %		4	2	2	1	0	1	2	3	1	2	1	2	3	0	1
N samples 10-20 %		1	3	1	0	3	0	2	0	0	3	2	3	2	0	2
N samples < 20 %		**5**	**5**	**3**	**1**	**3**	**1**	**4**	**3**	**1**	**5**	**3**	**5**	**5**	**0**	**3**
% of sample total < 20%		83	83	50	17	50	17	67	50	17	83	50	83	83	0	50

Table1: Duplicates from La Paz and Las Condes, fraction PM10 .

Percentage duplicates PM 2.5

Date	Sample	**Na**	**Mg**	**Al**	**P**	**K**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**
6/15/04	F2-661T	28.46	17.91	7.77	5.55	17.42	80.14	17.90	23.22	10.26	23.40	15.41	6.71	9.76	59.95	13.95	2.55	12.49	7.53	3.86
6/20/04	M1-0741	157.48	149.09	13.00	115.11	92.34	185.37	25.44	8.10	123.29	100.43	62.27	16.86	3.96	67.51	51.19	141.86	23.71	44.13	0.42
8/3/04	M1-1011	104.19	34.88	76.62	36.12	58.45	161.03	110.08	0.11	88.19	144.70	22.20	29.33	183.23	2.53	12.30	5.49	29.72	20.51	12.76
7/2/05	M1-0787	67.83	87.93	30.29	0.54	42.34	199.35	24.00	4.23	17.48	178.84	19.52	31.79	194.97	199.92	36.76	17.81	9.71	36.95	16.17
7/27/05	F1-0935	33.94	0.99	22.94	8.74	24.39	14.04	18.81	18.42	31.68	27.92	19.79	16.01	11.00	27.06	21.50	10.10	20.05	12.33	6.68
8/2/05	F1-0971-5	67.23	8.73	7.28	31.18	21.53	32.78	13.11	199.80	200.00	200.00	200.00	200.00	193.41	3.68	8.30	7.92	8.79	7.72	9.90
N samples : 0-10 %		0	2	2	3	0	0	0	3	0	0	0	1	2	2	1	3	2	2	4
N samples 10-20 %		0	1	1	0	1	1	3	1	2	0	3	2	1	0	2	2	1	1	2
N samples < 20 %		**0**	**3**	**3**	**3**	**1**	**1**	**3**	**4**	**2**	**0**	**3**	**3**	**3**	**2**	**3**	**5**	**3**	**3**	**6**
N samples % total < 20%		0	50	50	50	17	17	50	67	33	0	50	50	50	33	50	83	50	50	100

Percentage duplicates PM 2.5

Date	Sample	**Rb**	**Sr**	**Y**	**Zr**	**Mo**	**Ag**	**Cd**	**Sn**	**Sb**	**Cs**	**Ba**	**Pb**	**Bi**	**Th**	**U**
6/15/04	F2-661T	14.39	4.04	28.08	54.51	5.17	0.41	2.23	74.68	88.94	3.13	20.75	3.10	0.18	82.31	43.76
6/20/04	M1-0741	45.44	152.50	72.08	139.63	0.09	132.19	11.29	7.57	195.82	12.99	11.96	18.18	2.22	80.67	197.39
8/3/04	M1-1011	31.17	30.68	19.65	35.74	10.88	1.45	43.86	19.60	181.61	3.49	11.36	13.44	24.01	63.47	57.29
7/2/05	M1-0787	30.82	92.59	51.89	35.55	12.25	27.73	8.97	19.10	197.65	22.70	26.23	12.44	13.28	34.85	98.62
7/27/05	F1-0935	20.83	13.67	23.69	34.29	13.67	18.58	5.18	10.89	6.95	9.39	14.39	8.17	6.81	72.81	89.54
8/2/05	F1-0971-5	11.67	12.75	34.36	23.13	7.45	199.45	9.19	30.59	14.83	7.08	9.52	7.88	9.68	8.06	21.89
N samples : 0-10 %		0	1	0	0	3	2	4	1	1	4	1	3	4	1	0
N samples 10-20 %		2	2	1	0	3	1	1	3	1	1	3	3	1	0	0
N samples < 20 %		**2**	**3**	**1**	**0**	**6**	**3**	**5**	**4**	**2**	**5**	**4**	**6**	**5**	**1**	**0**
N samples % total < 20%		33	50	17	0	100	50	83	67	33	83	67	100	83	17	0

Table1 (continued): Duplicates from La Paz and Las Condes, fraction PM2.5.

Paz Station					
DATE	**SAMPLE PM2.5**	**SAMPLE PM10**	**PM2.5 (µg/m^3)**	**PM10 (µg/m^3)**	**Total (µg/m^3)**
20040113	F1-0025	F3-0026	20.1	38.9	58.9
20040125	F1-0049	F3-0050	13.4	25.8	39.2
20040218	F1-0103	F3-0104	22.8	50.8	73.7
20040227	F1-0123	F3-0124	11.9	23.7	35.6
20040325	F1-0201	F3-0202	34.7	55.1	89.8
20040331	F1-0219	F3-0220	12.3	27.0	39.3
20040413	F1-0303	F3-0304	10.7	16.6	27.3
20040429	F1-0399	F3-0400	83.5	40.8	124.2
20040430	F1-0405	F3-0406	84.4	51.2	135.5
20040506	F1-0441	F3-0442	80.1	50.8	131.0
20040507	F1-0453	F3-0454	85.6	65.4	151.0
20040517	F1-0513	F3-0514	138.2	81.5	219.6
20040518	F1-0519	F3-0520	111.0	58.1	169.1
20040521	F1-0539	F3-0540	21.1	15.2	36.3
20040530	F1-0601	F3-0602	85.8	36.4	122.2
20040531	F1-0607	F3-0608	117.9	61.5	179.4
20040603	F1-0631	F3-0632	84.2	62.0	146.2
20040615	F1-0707	F3-0708	83.6	68.5	152.1
20040620	F1-0737	F3-0738	16.0	10.3	26.3
20040713	F1-0879	F3-0880	16.6	5.4	22.0
20040716	F1-0897	F3-0898	102.2	44.0	146.2
20040729	F1-0977	F3-0978	62.5	64.4	126.9
20040803	F1-1007	F3-1008	11.6	8.1	19.7
20040823	F1-1127	F3-1128	46.9	52.9	99.7
20040826	F1-1145	F3-1146	64.7	36.7	101.4
20040902	F1-1187	F3-1188	65.5	62.7	128.2
20040918	F1-1283	F3-1284	8.4	9.1	17.5
20041002	F1-1361	F3-1362	20.1	38.3	58.4
20041012	F1-1391	F3-1392	5.2	15.8	21.0
20041111	F1-1469	F3-1470	25.5	55.2	80.7
20041114	F1-1475	F3-1476	12.7	17.4	30.1
20041205	F1-1517	F3-1518	11.0	18.2	29.2
20041229	F1-1565	F3-1566	22.4	36.0	58.4
20050107	F1-0013	F3-0014	42.1	27.2	69.3

Table 2: Analytical data (gravimetric data) from La Paz station. PM10, PM2.5 and total mass for both fractions in µg/m^3

Paz Station					
DATE	SAMPLE PM2.5	SAMPLE PM10	PM2.5 ($\mu g/m^3$)	PM10 ($\mu g/m^3$)	Total ($\mu g/m^3$)
20050131	F1-0067	F3-0068	16.7	19.0	35.7
20050203	F1-0073	F3-0074	31.4	41.4	72.8
20050212	F1-0091	F3-0092	17.6	17.9	35.6
20050326	F1-0199	F3-0200	12.8	14.5	27.4
20050330	F1-0211	F3-0212	33.2	53.9	87.2
20050410	F1-0271	F3-0272	22.8	27.1	49.9
20050415	F1-0301	F3-0302	63.4	72.6	136.0
20050429	F1-0393	F3-0394	68.0	65.0	133.0
20050504	F1-0423	F3-0424	11.8	13.6	25.4
20050526	F1-0562	F3-0563	82.1	72.4	154.5
20050527	F1-0568	F3-0569	74.0	76.8	150.8
20050528	F1-0574	F3-0575	67.2	49.2	116.4
20050530	F1-0586	F3-0587	71.4	66.2	137.6
20050607	F1-0642	F3-0643	102.8	65.1	167.9
20050608	F1-0648	F3-0649	92.1	51.8	143.9
20050622	F1-0723	F3-0724	67.7	82.6	150.3
20050627	F1-0753	F3-0754	12.3	4.5	16.8
20050709	F1-0823	F3-0824	75.3	60.2	135.5
20050714	F1-0853	F3-0854	17.1	16.6	33.7
20050727	F1-0935	F3-0936	109.5	96.5	206.1
20050728	F1-0941	F3-0942	91.1	65.0	156.2
20050802	F1-0971	F3-0972	61.2	48.9	110.1
20050810	F1-1025	F3-1026	88.9	68.6	157.5
20050818	F1-1073	F3-1074	55.2	66.2	121.4
20050821	F1-1091	F3-1092	9.5	10.8	20.3
20050917	F1-1229	F3-1230	65.0	43.5	108.5
20050927	F1-1289	F3-1290	105.8	28.0	133.7
20050928	F1-1295	F3-1296	13.5	17.1	30.5
20051002	F1-1313	F3-1314	14.0	9.5	23.5
20051020	F1-1367	F3-1368	30.7	44.7	75.4
20051111	F1-1421	F3-1422	23.1	47.4	70.5
20051123	F1-1445	F3-1446	3.8	11.1	14.9
20051208	F1-1475	F3-1476	10.0	23.1	33.1
20051214	F1-1487	F3-1488	21.0	56.8	77.8

Table 2 (continued): Analytical data (gravimetric data) from La Paz station. PM10, PM2.5 and total mass for both fractions in $\mu g/m^3$

Las Condes Station					
DATE	**SAMPLE PM2.5**	**SAMPLE PM10**	**PM2.5 ($\mu g/m^3$)**	**PM10 ($\mu g/m^3$)**	**Total ($\mu g/m^3$)**
20040113	M1-0029	M3-0030	19	47	66
20040125	M1-0053	M3-0054	13	24	37
20040203	M1-0077	M3-0078	38	35	72
20040227	M1-0071E	M3-0072E	12	25	37
20040323	M1-0199	M3-0200	28	45	74
20040331	M1-0223	M3-0224	6	8	15
20040422	M1-0361	M3-0362	9	10	19
20040429	M1-0403	M3-0404	68	29	97
20040510	M1-0475	M3-0476	95	44	139
20040517	M1-0517	M3-0518	81	68	149
20040519	M1-0531	M3-0532	110	52	162
20040522	M1-0549	M3-0550	12	10	21
20040620	M1-0741	M3-0742	13	7	20
20040624	M1-0769	M3-0770	76	42	118
20040712	M1-0877	M3-0878	76	27	103
20040716	M1-0901	M3-0902	60	38	98
20040721	M1-0931	M3-0932	8	7	16
20040803	M1-1011	M3-1012	7	5	12
20040825	M1-1143	M3-1144	41	34	75
20040827	M1-1155	M3-1156	56	43	99
20040902	M1-1191	M3-1192	45	50	96
20040907	M1-1221	M3-1222	8	8	16
20040914	M1-1263	M3-1264	43	36	78
20041002	M1-0469-E	M3-0470-E	19	35	55
20041004	M1-1371	M3-1372	27	44	71
20041012	M1-1395	M3-1396	7	12	18
20041102	M1-1455	M3-1456	13	36	50
20041108	M1-1467	M3-1468	16	27	43
20041114	M1-1479	M3-1480	9	13	22
20041205	M1-1521	M3-1522	12	21	33
20041217	M1-1545	M3-1546	14	34	48
20041226	M1-1563	M3-1564	19	30	49
20050107	M1-0017	M3-0018	28	31	59

Table 3: Analytical data (gravimetric data) from Las Condes station. PM10, PM2.5 and total mass for both fractions in $\mu g/m^3$.

Las Condes Station					
DATE	**SAMPLE PM2.5**	**SAMPLE PM10**	**PM2.5 (µg/m^3)**	**PM10 (µg/m^3)**	**Total (µg/m^3)**
20050131	M1-0071	M3-0072	8	22	30
20050203	M1-0077	M3-0078	32	43	75
20050206	M1-0083	M3-0084	21	22	44
20050212	M1-0095	M3-0096	28	17	45
20050330	M1-0215	M3-0216	38	65	104
20050402	M1-0227	M3-0228	15	22	37
20050423	M1-0353	M3-0354	47	46	94
20050427	M1-0381	M3-0382	58	31	89
20050502	M1-0415	M3-0416	69	37	106
20050523	M1-0544	M3-0545	6	5	11
20050531	M1-0596	M3-0597	58	37	94
20050606	M1-0636	M3-0637	54	30	84
20050625	M1-0745	M3-0746	78	38	116
20050627	M1-0757	M3-0758	8	2	11
20050702	M1-0787	M3-0788	15	5	19
20050728	M1-0945	M3-0946	69	54	123
20050729	M1-0951	M3-0952	101	47	148
20050810	M1-1029	M3-1030	74	48	122
20050812	M1-1041	M3-1042	67	53	120
20050816	M1-1065	M3-1066	4	2	7
20050903	M1-1161	M3-1162	17	6	23
20050905	M1-1167	M3-1168	65	41	107
20050917	M1-1233	M3-1234	65	36	100
20051008	M1-1335	M3-1336	31	32	63
20051018	M1-1365	M3-1366	23	46	70
20051024	M1-1383	M3-1384	15	11	26
20051108	M1-1419	M3-1420	24	52	76
20051111	M1-1425	M3-1426	26	60	86
20051123	M1-1449	M3-1450	6	8	14
20051208	M1-1479	M3-1480	11	20	31
20051223	M1-1509	M3-1510	22	48	70

Table 3 (continued): Analytical data (gravimetric data) from Las Condes station. PM10, PM2.5 and total mass for both fractions in µg/m^3.

Table (4-a): La Paz (PM 2.5) ng/m^3

date	Na	Mg	Al	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
13/01/2004	217,98	19,77	59,94	5,30	161,75	175,17	0,01	4,18	0,47	0,49	2,58	68,94	-	0,02	8,27	16,51	0,02
25/01/2004	107,08	11,30	38,10	-	33,16	131,51	0,01	2,74	0,19	0,13	1,58	49,09	-	-	4,63	1,62	0,02
18/02/2004	1387,45	316,81	342,00	37,02	643,45	3116,99	0,08	0,01	1,36	16,14	25,60	496,07	0,004	11,80	44,84	58,38	0,16
27/02/2004	111,22	11,10	37,97	2,78	52,31	156,61	0,005	2,91	0,29	0,42	1,79	54,44	0,01	0,004	1,80	0,39	0,02
25/03/2004	455,84	79,26	423,76	25,73	838,50	256,06	0,10	0,01	1,53	0,07	15,17	497,20	0,004	0,005	18,36	44,62	0,18
31/03/2004	321,38	43,09	134,28	26,25	169,18	712,66	0,03	0,01	0,43	0,06	10,01	294,13	0,003	0,004	29,90	36,69	0,12
13/04/2004	5,10	-	1,96	-	-	-	-	0,32	0,02	-	0,53	13,08	-	-	2,66	-	0,004
29/04/2004	12,64	1,24	7,91	-	55,46	-	-	0,78	0,11	-	1,68	43,18	-	-	4,92	-	0,02
30/04/2004	16,86	2,41	13,06	-	52,10	-	-	1,38	0,12	2,24	2,20	50,74	-	-	5,78	5,37	0,03
06/05/2004	3,19	-	-	-	19,67	-	-	0,58	0,10	-	1,33	26,23	-	-	2,73	-	0,01
07/05/2004	14,83	1,49	6,99	-	31,08	-	-	1,02	0,11	0,40	3,52	68,69	-	-	8,86	5,51	0,03
21/05/2004	6,41	-	-	-	-	-	-	0,23	0,08	-	1,78	58,51	-	-	10,14	-	0,02
30/05/2004	9,69	0,56	2,41	-	27,51	-	-	0,45	0,12	-	2,07	35,26	-	-	4,57	0,17	0,02
31/05/2004	9,34	0,34	3,04	-	23,94	-	-	0,78	0,07	-	2,38	47,44	-	-	4,64	3,75	0,04
15/06/2004	112,61	33,80	104,66	21,77	326,04	281,43	0,03	10,93	0,57	6,60	31,85	384,56	0,21	1,04	59,89	115,21	0,30
20/06/2004	43,15	11,39	11,81	9,94	94,94	38,16	-	2,39	0,21	1,11	3,35	95,89	0,03	0,34	11,80	22,73	0,04
13/07/2004	66,86	8,70	34,13	8,66	116,06	5,31	0,001	1,93	0,10	0,66	5,47	110,26	0,01	0,25	8,09	32,03	0,05
16/07/2004	111,90	9,93	29,88	29,17	216,68	130,25	0,02	0,91	0,14	3,26	37,96	107,25	3,52	0,87	12,18	73,93	0,09
29/07/2004	237,75	85,31	350,64	38,63	398,32	454,94	0,07	29,52	1,14	20,79	50,82	1167,90	0,31	2,72	71,10	174,81	0,52
03/08/2004	58,92	13,65	125,33	7,70	79,20	66,71	0,01	5,01	0,52	2,89	5,92	166,68	0,27	0,48	8,31	16,98	0,06
23/08/2004	145,65	51,82	302,68	20,46	304,27	233,12	0,05	20,64	0,68	4,24	24,17	534,50	0,16	0,85	44,24	101,55	0,34
26/08/2004	313,02	39,04	153,01	29,19	453,69	199,47	0,03	18,53	2,95	15,85	55,45	823,90	0,82	5,48	65,03	229,74	0,52
02/09/2004	27,23	7,14	53,40	13,26	58,00	39,80	0,01	2,74	0,16	1,43	5,04	95,34	24,76	0,35	8,03	22,49	0,06
18/09/2004	84,71	4,93	9,68	25,75	108,72	78,32	0,02	0,03	0,04	0,69	40,61	2,99	4,28	0,41	1,64	30,56	0,005
02/10/2004	25,15	4,70	25,57	34,41	44,30	20,32	0,02	0,68	0,12	1,66	42,50	29,44	4,34	0,09	2,80	5,88	0,02
07/01/2005	303,68	32,26	91,02	2,89	467,30	104,66	0,01	6,68	0,26	0,26	3,34	100,38	-	-	3,15	5,16	0,03

Table 4-a: Chemical data for major and trace element. PM2,5 at La Paz station. Date: 13/01/2004 - 07/01/2005.

Table (4-a): La Paz (PM 2.5) ng/m^3

date	Na	Mg	Al	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
31/01/2005	194,32	22,95	88,56	4,52	164,39	274,24	0,01	5,80	0,23	0,39	7,28	100,91	-	-	5,56	21,02	0,03
12/02/2005	196,20	17,34	54,39	0,38	78,39	84,35	-	2,18	0,27	0,07	0,96	41,31	-	-	7,40	-	0,02
26/03/2005	370,18	67,48	26,20	2,99	211,83	931,04	-	2,01	0,32	3,03	4,41	52,86	-	2,38	8,41	6,24	0,02
30/03/2005	179,59	16,03	77,67	1,42	191,98	295,45	0,01	6,79	0,59	0,75	6,05	132,34	0,004	-	11,28	13,11	0,05
10/04/2005	16,97	-	-	-	15,20	-	-	0,62	0,25	0,24	0,41	23,87	-	-	1,92	-	0,01
15/04/2005	32,63	10,61	59,64	0,78	67,21	2,43	0,003	4,19	0,38	0,22	5,68	131,23	-	-	8,28	6,35	0,04
26/05/2005	8,39	0,62	6,57	-	7,11	-	-	1,16	0,14	0,08	2,58	38,01	-	-	2,81	3,70	0,03
27/05/2005	12,99	2,41	11,65	-	27,49	-	-	1,72	0,13	0,22	9,19	79,20	-	-	4,33	13,92	0,04
30/05/2005	138,72	7,95	34,89	11,89	97,82	87,03	0,01	6,63	0,54	3,26	17,48	255,46	0,10	0,84	16,81	28,26	0,15
07/06/2005	209,54	57,74	181,29	35,53	556,03	408,58	0,05	19,07	4,48	13,24	53,03	853,09	0,64	5,47	80,88	242,50	0,51
08/06/2005	139,46	40,54	121,99	29,15	399,86	393,94	0,02	11,48	2,40	7,93	26,99	536,48	0,24	2,64	41,76	104,64	0,28
22/06/2005	1121,63	391,01	163,59	37,42	405,53	3547,58	0,04	18,60	1,42	10,01	73,76	770,26	0,41	6,73	57,93	142,31	0,36
27/06/2005	21,49	6,09	17,40	4,55	49,28	173,40	0,004	2,39	0,72	1,43	5,92	83,71	0,06	0,16	9,61	15,46	0,05
09/07/2005	101,63	32,85	72,56	8,45	124,29	342,57	0,02	7,95	0,52	2,88	12,31	277,06	0,09	0,20	14,25	43,70	0,12
14/07/2005	61,54	23,89	63,17	8,92	134,98	201,11	0,01	6,29	0,45	4,03	18,84	331,03	0,26	0,37	23,92	89,84	0,12
27/07/2005	273,32	92,27	326,89	57,51	604,16	593,73	0,07	33,24	4,01	15,11	65,35	1077,54	0,66	6,25	116,88	286,19	0,61
28/07/2005	101,89	30,68	99,72	27,44	221,18	154,20	-	17,01	1,18	6,58	33,01	424,92	0,27	3,44	34,36	151,61	0,28
02/08/2005	544,40	65,97	217,97	53,56	712,97	424,77	0,04	0,01	1,09	12,54	69,43	1088,49	0,004	3,55	93,22	328,60	0,59
10/08/2005	591,00	443,30	2477,35	77,59	608,91	2489,19	-	206,55	5,20	9,89	59,80	2500,05	1,12	2,92	67,38	85,47	0,65
18/08/2005	96,97	46,84	146,61	36,34	227,22	307,20	0,03	15,82	0,56	7,01	48,83	686,40	0,22	1,74	48,10	117,13	0,30
21/08/2005	124,08	13,47	23,95	5,14	78,16	-	0,003	1,76	0,28	0,80	2,64	91,41	-	0,29	17,00	21,43	0,04
17/09/2005	52,77	5,74	23,13	14,35	92,69	26,99	0,02	2,14	0,19	1,20	1,05	41,77	31,58	0,25	4,75	8,56	0,02
27/09/2005	23,91	2,86	13,53	31,34	24,64	21,99	0,01	0,22	0,09	1,00	41,62	27,56	4,33	0,18	3,45	10,83	0,02
02/10/2005	23,57	2,25	3,92	29,93	12,24	14,92	0,01	0,07	0,14	0,64	39,70	11,61	0,00	0,11	0,98	1,29	0,005
20/10/2005	51,51	7,11	25,74	12,78	30,06	25,55	0,02	20,27	0,32	19,46	6,52	111,97	26,77	63,04	3,50	8,07	0,02

Table 4-a (continued): Chemical data for major and traces elements. PM2,5 at La Paz station. Date: 31/01/2005 - 20/10/2005.

Table (4-a): La Paz (PM 2.5) ng/m^3

date	**Ge**	**As**	**Rb**	**Sr**	**Zr**	**Mo**	**Ag**	**Cd**	**Sn**	**Sb**	**Cs**	**Ba**	**Hf**	**W**	**Pb**	**Bi**	**U**
13/01/2004	0,01	0,93	0,19	0,44	0,10	1,07	0,08	0,05	1,86	-	0,01	4,56	-	-	3,54	0,02	-
25/01/2004	0,002	0,28	0,09	0,29	1,25	0,74	0,03	0,03	1,20	-	0,003	4,53	0,02	-	1,88	0,01	-
18/02/2004	8,51	6,86	1,04	10,92	0,67	4,93	0,00	0,23	2,58	0,005	0,05	44,50	0,0004	0,03	12,71	0,23	0,02
27/02/2004	0,005	0,33	0,09	0,31	0,20	0,14	0,03	0,04	4,23	0,004	0,004	4,57	0,0003	0,08	1,62	0,02	0,0002
25/03/2004	0,05	2,85	1,93	2,28	0,87	2,66	0,001	0,56	12,85	0,004	0,06	45,07	0,02	0,21	16,59	0,05	0,01
31/03/2004	0,04	4,35	0,30	1,45	1,73	6,67	0,001	0,17	4,41	0,004	0,02	38,08	0,03	0,14	10,75	0,04	0,003
13/04/2004	0,001	0,08	0,02	0,01	-	0,31	0,28	0,02	0,30	-	0,001	1,50	-	-	0,84	0,003	-
29/04/2004	0,01	2,84	0,12	0,03	0,03	0,43	0,27	0,08	0,26	-	0,003	1,24	-	-	1,17	0,02	-
30/04/2004	0,01	2,52	0,13	0,14	0,04	0,56	0,43	0,07	0,91	-	0,004	5,22	-	-	4,35	0,02	-
06/05/2004	0,004	0,93	0,04	0,03	0,01	0,12	0,14	0,06	0,78	-	0,001	1,36	-	-	3,48	0,02	-
07/05/2004	0,01	2,01	0,05	0,13	0,07	0,54	0,17	0,10	0,85	-	0,003	3,04	-	-	6,79	0,05	-
21/05/2004	0,01	1,15	0,09	0,03	-	0,08	1,47	0,08	0,60	-	0,002	10,29	-	-	7,37	0,04	-
30/05/2004	0,01	1,36	0,08	0,07	0,02	0,35	0,37	0,07	1,00	-	0,003	5,15	-	-	4,49	0,04	-
31/05/2004	0,02	1,12	0,08	0,09	0,02	0,23	0,43	0,11	0,97	-	0,004	4,79	-	-	6,52	0,03	-
15/06/2004	0,12	14,07	0,68	1,24	0,57	5,48	0,32	0,93	9,45	8,06	0,06	27,56	0,01	0,10	57,20	0,42	0,01
20/06/2004	0,02	3,22	0,17	0,25	1,08	0,85	0,60	0,19	4,16	1,89	0,06	10,00	0,02	0,02	8,81	0,09	0,001
13/07/2004	0,02	4,36	0,25	0,28	0,18	0,28	0,08	0,25	2,27	-	0,01	12,01	-	0,08	13,48	0,04	-
16/07/2004	0,03	2,39	0,29	0,82	0,11	0,43	0,14	0,29	0,33	28,77	0,01	7,97	0,001	0,03	17,80	0,08	0,01
29/07/2004	0,18	18,31	0,93	3,10	2,57	4,82	0,35	1,56	10,22	7,19	0,08	107,18	0,05	0,31	52,97	0,30	0,02
03/08/2004	0,02	0,88	0,16	0,51	0,61	0,91	0,06	0,33	0,76	-	0,01	16,75	0,01	0,59	6,68	0,03	0,002
23/08/2004	0,14	8,32	0,65	1,71	1,93	2,07	0,24	0,46	3,93	2,92	0,04	45,08	0,03	0,31	43,61	0,19	0,01
26/08/2004	0,27	8,40	0,90	1,80	0,87	2,82	2,23	1,72	6,96	4,64	0,08	33,49	0,02	0,90	91,02	0,41	0,01
02/09/2004	0,02	3,40	0,11	0,32	0,20	0,71	0,13	0,15	0,68	80,95	0,01	8,47	0,003	0,02	5,89	0,05	0,003
18/09/2004	0,001	0,12	0,09	0,70	0,01	0,13	0,07	0,01	0,03	14,82	0,001	1,00	-	-	0,45	0,01	0,004
02/10/2004	0,01	0,82	0,10	0,72	0,04	0,12	0,10	0,04	0,47	55,05	0,004	2,26	0,0003	0,003	2,14	0,02	0,05
07/01/2005	0,01	0,35	0,58	0,63	0,13	1,97	0,05	0,09	1,26	-	0,01	6,24	-	0,01	2,70	0,01	-

Table 4-a (continued): Chemical data for major and traces elements. PM2,5 at La Paz station. Date: 13/01/2004 - 07/01/2005.

Table (4-a): La Paz (PM 2.5) ng/m^3

date	Ge	As	Rb	Sr	Zr	Mo	Ag	Cd	Sn	Sb	Cs	Ba	Hf	W	Pb	Bi	U
31/01/2005	0,01	0,71	0,21	0,61	0,18	0,35	0,03	0,04	1,05	-	0,01	7,68	-	0,003	2,02	0,03	0,003
12/02/2005	0,004	0,21	0,18	0,27	0,04	0,07	0,03	0,03	1,77	-	0,003	3,20	-	-	1,07	0,002	-
26/03/2005	0,01	0,56	0,22	2,52	0,05	0,20	0,04	0,08	3,66	-	0,01	3,97	-	-	3,60	0,03	-
30/03/2005	0,02	0,56	0,44	0,69	0,22	1,92	0,07	0,19	6,22	0,16	0,01	8,11	0,00	0,07	6,95	0,02	-
10/04/2005	0,004	0,18	0,05	0,01	0,00	0,16	0,06	0,01	0,98	-	0,001	0,31	-	-	0,49	0,01	-
15/04/2005	0,02	1,49	0,13	0,36	0,13	0,57	0,34	0,07	1,09	-	0,01	10,20	-	-	4,72	0,04	-
26/05/2005	0,01	0,39	0,04	0,06	0,03	0,10	0,29	0,11	0,39	-	0,003	2,31	-	-	3,00	0,02	-
27/05/2005	0,02	0,47	0,07	0,17	0,06	0,17	0,33	0,11	0,89	-	0,004	6,41	-	0,01	9,36	0,03	-
30/05/2005	0,08	3,14	0,16	0,56	0,34	0,83	1,68	0,23	2,70	0,81	0,02	8,45	0,004	0,10	10,50	0,12	0,0004
07/06/2005	0,27	16,36	1,23	2,25	1,20	6,51	0,28	1,53	18,79	8,79	0,09	57,89	0,03	0,31	92,39	0,43	0,01
08/06/2005	0,16	9,17	0,83	1,56	0,97	3,61	0,18	0,86	9,90	4,76	0,05	48,46	0,02	0,15	48,52	0,28	0,01
22/06/2005	0,15	9,57	0,69	12,92	1,13	7,71	0,44	0,74	9,02	4,49	0,04	69,40	0,03	0,19	50,90	0,34	0,02
27/06/2005	0,02	0,93	0,13	0,30	0,12	0,51	0,03	0,13	0,83	0,38	0,01	7,46	0,00	0,05	6,31	0,02	0,001
09/07/2005	0,07	4,10	0,25	1,21	0,37	0,89	0,10	0,33	5,83	1,29	0,01	27,91	0,01	0,04	17,87	0,16	0,004
14/07/2005	0,08	3,16	0,36	0,93	0,32	0,71	0,14	0,54	2,38	8,24	0,03	35,75	0,01	0,15	40,38	0,08	0,004
27/07/2005	0,30	11,46	1,32	3,36	1,71	7,04	0,93	1,99	27,66	16,76	0,11	73,51	0,04	0,53	113,99	0,28	0,02
28/07/2005	0,14	4,54	0,46	1,10	0,86	2,34	0,27	1,00	9,47	10,36	0,05	21,32	0,02	0,29	59,23	0,10	0,01
02/08/2005	0,26	13,78	1,33	3,11	4,52	7,53	0,001	2,16	19,35	8,96	0,07	81,84	0,09	0,23	97,15	0,87	0,01
10/08/2005	0,09	2,97	2,05	14,70	7,04	10,96	0,13	0,24	5,12	6,73	0,23	93,96	0,23	0,58	25,27	0,16	0,08
18/08/2005	0,12	8,12	0,53	1,87	0,87	5,96	0,69	1,79	10,28	6,87	0,04	66,39	0,02	0,20	39,71	0,20	0,01
21/08/2005	0,02	2,09	0,16	0,34	0,19	1,29	0,10	0,18	14,01	0,42	0,01	12,25	-	0,003	7,14	0,05	-
17/09/2005	0,01	1,56	0,22	0,20	0,11	0,29	0,10	0,11	0,77	124,17	0,02	5,30	0,002	0,01	3,53	0,02	0,002
27/09/2005	0,01	0,21	0,04	0,71	0,04	0,38	0,07	0,05	0,19	42,98	0,002	1,96	0,0004	0,004	1,45	0,03	0,003
02/10/2005	0,002	0,70	0,02	0,64	0,02	0,16	0,12	0,02	0,09	0,001	0,001	1,89	0,002	0,01	0,78	0,01	0,0003
20/10/2005	0,01	0,80	0,07	0,19	0,08	0,72	0,14	0,05	1,83	103,27	0,003	2,62	0,004	0,04	2,20	0,02	0,01

Table 4-a (continued): Chemical data for major and traces elements. PM2,5 at La Paz station. Date: 31/01/2005 - 20/10/2005.

Table (4-b): La Paz REEs (PM 2.5) ng/m^3

date	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Hf**	**W**
13/01/2004	0,03	0,06	0,006	0,02	0,004	0,001	0,004	0,001	0,003	0,0005	0,002	0,002	-	-
25/01/2004	0,02	0,04	0,004	0,01	0,004	0,001	0,003	0,0003	0,002	0,0004	0,001	0,002	0,02	-
18/02/2004	0,21	0,39	0,04	0,12	0,02	0,01	0,03	0,003	0,02	0,003	0,01	0,01	0,0004	0,03
27/02/2004	0,02	0,05	0,005	0,01	0,002	0,001	0,00	0,0003	0,002	0,0003	0,001	0,001	0,0003	0,08
25/03/2004	0,21	0,47	0,05	0,141	0,03	0,01	0,03	0,004	0,02	0,004	0,01	0,01	0,02	0,21
31/03/2004	0,12	0,25	0,02	0,06	0,01	0,01	0,01	0,0014	0,01	0,001	0,004	0,004	0,03	0,14
13/04/2004	0,004	0,01	0,001	-	-	-	-	-	-	-	-	-	-	-
29/04/2004	0,01	0,02	0,002	0,0004	0,0004	0,0001	0,0004	0,0001	0,0003	-	0,0005	0,0001	-	-
30/04/2004	0,02	0,06	0,004	0,004	0,001	0,001	0,001	0,0001	0,001	0,00001	0,0001	0,0003	-	-
06/05/2004	0,01	0,02	0,002	-	0,000	-	0,0001	0,000003	0,0001	-	-	0,0001	-	-
07/05/2004	0,03	0,08	0,006	0,007	0,001	0,0005	0,001	0,0001	0,001	0,0001	0,0003	0,0004	-	-
21/05/2004	0,03	0,07	0,005	-	-	0,0002	-	-	-	-	-	-	-	-
30/05/2004	0,02	0,04	0,003	0,002	0,0003	0,0004	0,0002	0,00003	0,0001	-	-	0,00005	-	-
31/05/2004	0,01	0,03	0,002	0,004	0,0004	0,0003	0,0003	0,00003	0,0001	-	-	0,00004	-	-
15/06/2004	0,12	0,31	0,02	0,05	0,01	0,01	0,012	0,0012	0,01	0,001	0,003	0,003	0,01	0,10
20/06/2004	0,04	0,09	0,006	0,01	0,001	0,001	0,001	0,0001	-	-	-	-	0,02	0,02
13/07/2004	0,05	0,12	0,008	0,01	0,002	0,002	0,002	0,0002	0,001	0,0001	0,001	0,0004	-	0,08
16/07/2004	0,05	0,12	0,008	0,02	0,002	0,001	0,004	0,0004	0,001	0,0003	0,001	0,001	0,001	0,03
29/07/2004	0,32	0,91	0,06	0,16	0,02	0,02	0,03	0,0030	0,02	0,003	0,01	0,01	0,05	0,31
03/08/2004	0,05	0,12	0,008	0,02	0,004	0,002	0,004	0,0004	0,002	0,0004	0,001	0,001	0,01	0,59
23/08/2004	0,21	0,81	0,03	0,10	0,02	0,01	0,02	0,0024	0,01	0,002	0,01	0,01	0,03	0,31
26/08/2004	0,26	0,48	0,03	0,09	0,02	0,01	0,02	0,0016	0,01	0,002	0,004	0,004	0,02	0,90
02/09/2004	0,05	0,13	0,007	0,02	0,002	0,001	0,004	0,0003	0,002	0,0003	0,001	0,001	0,003	0,02
18/09/2004	0,01	0,01	0,001	0,002	0,0004	0,0002	0,001	0,0001	0,000	0,0000	0,0001	0,0001	-	-
02/10/2004	0,02	0,04	0,003	0,008	0,001	0,001	0,002	0,0002	0,001	0,0002	0,001	0,001	0,0003	0,003
07/01/2005	0,05	0,09	0,01	0,03	0,01	0,002	0,01	0,0008	0,005	0,001	0,003	0,002	-	0,01

Table 4-b: Chemical data for REEs elements. PM2,5 at La Paz station. Date: 13/01/2004 -07/01/2005.

Table (4-b): La Paz REEs (PM 2.5) ng/m^3

date	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Hf**	**W**
31/01/2005	0,05	0,10	0,01	0,03	0,01	0,002	0,01	0,001	0,005	0,001	0,002	0,002	-	0,003
12/02/2005	0,02	0,04	0,004	0,01	0,002	0,001	0,002	0,0002	0,001	0,0003	0,001	0,001	-	-
26/03/2005	0,04	0,04	0,01	0,01	0,003	0,001	0,005	0,0003	0,002	0,0002	0,001	0,001	-	-
30/03/2005	0,06	0,11	0,01	0,03	0,01	0,002	0,01	0,001	0,005	0,001	0,003	0,003	0,0003	0,07
10/04/2005	0,004	0,01	0,001	-	0,0003	-	0,00002	0,00002	0,000	-	-	0,0002	-	-
15/04/2005	0,06	0,12	0,008	0,02	0,004	0,002	0,004	0,0004	0,002	0,0004	0,001	0,001	-	-
26/05/2005	0,01	0,02	0,002	-	0,0004	0,000	0,001	0,00002	0,0003	-	-	0,0001	-	-
27/05/2005	0,04	0,07	0,004	0,01	0,001	0,001	0,002	0,0001	0,001	0,00003	0,0002	0,0003	-	0,01
30/05/2005	0,07	0,14	0,01	0,03	0,01	0,002	0,01	0,001	0,003	0,0005	0,002	0,001	0,004	0,10
07/06/2005	0,44	0,76	0,06	0,20	0,03	0,01	0,04	0,003	0,01	0,002	0,01	0,01	0,03	0,31
08/06/2005	0,31	0,51	0,04	0,11	0,01	0,01	0,03	0,002	0,01	0,002	0,01	0,01	0,02	0,15
22/06/2005	0,39	0,74	0,05	0,15	0,02	0,01	0,03	0,002	0,01	0,002	0,01	0,004	0,03	0,19
27/06/2005	0,07	0,12	0,01	0,02	-	0,001	0,01	0,0003	0,001	0,0003	0,001	0,0004	0,003	0,05
09/07/2005	0,12	0,21	0,02	0,08	0,01	0,01	0,01	0,001	0,004	0,001	0,003	0,002	0,01	0,04
14/07/2005	0,11	0,24	0,02	0,05	0,004	0,01	0,01	0,001	0,003	0,001	0,002	0,002	0,01	0,15
27/07/2005	0,51	0,89	0,06	0,19	0,03	0,02	0,05	0,004	0,02	0,004	0,01	0,01	0,04	0,53
28/07/2005	0,14	0,24	0,02	0,06	0,01	0,004	0,01	0,005	0,001	0,003	0,0001	0,002	0,02	0,29
02/08/2005	0,40	0,90	0,05	0,13	0,02	0,01	0,03	0,002	0,01	0,002	0,01	0,01	0,09	0,23
10/08/2005	0,83	1,83	0,20	0,78	0,17	0,05	0,18	0,143	0,03	0,087	0,005	0,08	0,23	0,58
18/08/2005	0,29	0,65	0,04	0,11	0,01	0,01	0,02	0,002	0,01	0,002	0,01	0,005	0,02	0,20
21/08/2005	0,08	0,10	0,01	0,02	0,005	0,002	0,004	0,0002	0,002	0,0002	0,001	0,001	-	0,003
17/09/2005	0,05	0,09	0,005	0,01	0,002	0,001	0,00	0,0002	0,001	0,0002	0,0005	0,0005	0,002	0,01
27/09/2005	0,02	0,02	0,002	0,01	0,001	0,0004	0,001	0,0001	0,0004	0,0001	0,0003	0,0003	0,0004	0,004
02/10/2005	0,03	0,02	0,002	0,01	0,001	0,0003	0,001	0,00005	0,0003	0,00001	0,0001	0,00003	0,002	0,01
20/10/2005	0,04	0,05	0,004	0,01	0,003	0,001	0,003	0,0002	0,001	0,0002	0,001	0,001	0,004	0,04

Table 4-b (continued): Chemical data for REEs elements. PM2,5 at La Paz station. Date: 31/01/2005 - 20/10/2005.

Table (4-c): La Paz (PM 10) ng/m^3

date	Na	Mg	Al	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
13/01/2004	319,06	81,37	602,68	19,19	154,05	501,39	0,14	46,21	1,20	1,10	12,52	457,01	0,13	-	8,66	6,91	0,16
25/01/2004	209,59	61,72	359,05	9,57	87,06	232,37	0,07	23,50	0,64	0,21	7,14	268,98	0,02	-	5,87	6,27	0,09
18/02/2004	336,74	118,01	766,21	20,81	203,98	685,83	0,17	53,32	1,37	1,31	15,77	624,43	0,18	0,06	12,45	7,48	0,19
27/02/2004	198,88	56,57	354,91	8,76	91,90	362,75	0,08	23,53	0,70	0,34	7,53	288,74	0,06	-	7,03	-	0,09
25/03/2004	1418,55	578,20	3894,86	121,41	956,09	2831,49	0,83	737,35	9,18	581,15	108,77	4715,42	10,60	887,52	56,95	157,93	0,91
31/03/2004	230,67	68,64	371,95	10,53	85,96	432,03	0,08	27,38	0,74	1,94	8,19	365,53	0,06	0,59	8,92	4,05	0,09
13/04/2004	19,75	10,10	64,49	-	4,59	25,45	0,01	4,35	0,11	-	1,37	58,41	-	-	2,41	-	0,01
29/04/2004	75,12	35,27	215,32	2,09	49,53	160,71	0,04	15,80	0,39	0,54	4,68	208,03	0,01	-	8,00	0,40	0,05
30/04/2004	67,44	32,99	182,49	2,30	47,88	165,04	0,03	17,24	0,44	0,66	5,27	229,69	0,003	-	8,28	5,77	0,06
06/05/2004	61,13	35,28	220,69	2,36	47,85	190,65	0,04	15,46	0,38	0,44	4,64	200,79	0,03	-	6,50	3,20	0,05
07/05/2004	61,71	21,33	135,91	3,33	49,96	153,50	0,02	15,41	0,46	0,79	5,79	234,76	0,03	-	15,32	3,34	0,06
18/05/2004	55,79	23,07	173,84	1,94	43,91	151,19	0,03	14,55	0,35	0,25	4,42	181,62	0,02	-	7,14	0,27	0,05
21/05/2004	2,50	-	42,82	-	-	8,68	0,002	2,99	0,08	-	0,89	47,14	-	-	1,92	-	0,01
30/05/2004	49,29	26,07	136,75	0,29	27,49	112,54	0,02	0,01	0,27	1,11	3,55	170,38	-	-	7,23	2,39	0,03
31/05/2004	67,44	33,89	211,66	2,95	49,33	249,10	0,04	18,30	0,42	0,73	5,42	250,06	0,04	0,003	6,79	3,59	0,06
15/06/2004	1104,74	621,84	3890,55	114,08	944,92	4212,15	0,82	310,72	6,58	26,67	96,18	3719,91	1,77	5,24	130,44	141,19	0,92
20/06/2004	123,56	75,01	290,09	19,44	96,53	311,80	-	30,83	0,74	1,74	9,64	439,54	0,15	0,45	13,73	19,26	0,09
13/07/2004	85,55	26,69	117,34	6,13	42,57	139,39	0,02	9,14	0,23	1,42	4,32	259,14	0,04	0,42	8,68	8,14	0,03
16/07/2004	442,61	291,69	1663,19	51,67	413,60	1796,95	0,36	138,88	3,17	9,61	45,40	2064,25	0,83	1,88	52,39	77,66	0,45
29/07/2004	561,50	257,39	1715,96	63,25	490,91	1948,67	0,37	182,95	4,29	8,54	49,61	2211,25	0,87	1,91	52,01	63,25	0,53
03/08/2004	149,01	72,53	434,15	13,05	105,09	525,69	0,08	35,16	0,91	3,06	9,33	448,26	0,33	0,47	10,46	7,85	0,09
23/08/2004	729,84	364,29	2271,44	87,48	632,44	2046,76	0,43	209,45	5,15	10,15	73,30	2909,31	1,08	2,61	64,58	84,04	0,64
26/08/2004	330,57	157,75	1023,37	44,73	328,36	1182,06	0,22	114,74	3,05	6,73	32,98	1369,17	0,58	3,13	37,28	55,80	0,33
02/09/2004	192,70	73,51	628,61	18,31	162,20	619,26	0,13	27,18	1,11	2,88	14,70	583,69	27,60	0,88	16,39	24,91	0,16
18/09/2004	86,76	7,91	31,81	27,63	17,42	36,61	0,01	1,85	0,09	0,42	32,59	37,93	3,35	0,08	1,10	1,16	0,01
02/10/2004	119,83	8,02	207,94	38,97	82,97	175,54	0,04	14,91	0,58	1,18	40,93	236,67	3,75	0,69	4,41	9,10	0,08
12/10/2004	146,62	24,57	98,86	36,24	35,97	123,90	0,03	5,88	0,20	1,41	41,35	97,96	4,17	0,17	3,00	6,31	0,03

Table 4-c: Chemical data for major and traces elements. PM10 at La Paz station. Date: 13/01/2004 - 12/10/2004

Table (4-c): La Paz (PM 10) ng/m^3

date	Na	Mg	Al	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
07/01/2005	314,61	63,96	287,86	7,64	104,68	266,14	0,06	20,05	0,52	0,03	6,00	220,94	-	-	3,46	-	0,07
31/01/2005	209,03	46,54	237,54	3,67	64,64	300,46	0,05	14,82	0,45	0,21	8,04	213,45	-	-	5,09	5,25	0,06
03/02/2005	758,41	66,05	403,07	15,80	205,38	461,90	0,08	35,36	1,12	0,40	12,00	409,23	0,12	-	10,31	14,00	0,14
12/02/2005	100,26	27,49	172,78	2,02	55,31	246,84	0,03	15,03	0,34	-	3,68	139,53	-	-	3,43	2,48	0,04
26/03/2005	217,13	37,27	154,49	4,48	52,85	155,37	0,04	10,06	0,33	0,80	3,10	126,42	-	-	13,34	1,61	0,04
30/03/2005	471,00	82,78	655,45	21,94	220,66	575,69	0,13	58,91	1,55	8,34	16,78	590,14	0,26	-	12,88	11,12	0,18
10/04/2005	69,94	24,34	147,93	-	27,60	63,88	0,02	9,30	0,34	0,05	2,83	119,01	-	-	2,16	-	0,03
15/04/2005	76,87	29,48	190,43	3,45	57,40	174,69	0,03	19,96	0,56	0,44	7,90	286,50	0,03	-	7,68	0,63	0,07
29/04/2005	80,16	46,83	287,28	4,68	60,23	242,74	0,05	22,18	0,61	0,92	7,16	346,91	0,05	-	9,97	3,09	0,07
27/05/2005	937,01	306,35	2041,16	80,45	737,36	3149,03	0,39	226,69	5,99	19,05	145,68	3655,02	1,54	4,48	85,86	132,51	0,74
07/06/2005	523,83	256,82	1675,92	76,28	495,54	2249,79	0,38	155,13	5,43	21,43	52,53	2335,56	1,05	5,28	58,57	90,31	0,50
08/06/2005	316,87	180,53	956,68	46,10	305,81	1266,94	0,22	94,56	3,05	15,34	34,20	1468,13	0,61	5,88	38,78	55,20	0,29
22/06/2005	917,86	248,15	2420,07	106,04	896,62	2419,22	0,52	308,26	8,25	20,64	149,53	3618,70	2,24	13,06	80,00	104,82	0,85
27/06/2005	37,18	18,41	88,47	6,70	42,43	141,00	0,02	8,23	0,38	1,46	6,28	208,68	0,04	0,33	7,37	3,90	0,03
09/07/2005	572,15	119,66	1379,12	70,79	522,02	1187,21	0,29	168,14	4,58	10,13	49,79	2378,45	0,84	3,11	56,83	69,15	0,52
14/07/2005	192,03	134,32	671,66	16,39	148,58	924,71	0,12	46,92	1,39	4,24	23,22	793,41	0,32	0,40	16,12	26,71	0,15
27/07/2005	489,39	206,22	1456,77	43,33	373,22	1491,62	0,31	114,01	3,22	6,37	33,91	1367,47	0,66	1,53	32,38	37,48	0,35
28/07/2005	641,93	293,30	1706,85	89,90	640,01	2175,37	-	178,56	3,77	9,37	52,17	1677,73	1,08	2,67	42,23	100,40	0,49
02/08/2005	260,62	100,44	655,29	17,98	155,28	834,80	0,13	55,82	1,25	3,60	18,52	760,57	0,20	0,21	17,94	27,10	0,15
10/08/2005	476,89	357,71	1999,02	62,61	491,34	2008,58	-	166,67	4,19	7,98	48,25	2017,34	0,90	2,36	54,37	68,97	0,52
18/08/2005	726,21	231,63	2128,54	75,11	677,57	1743,14	0,41	228,42	5,51	7,90	62,71	2670,82	1,19	2,10	56,68	77,70	0,78
21/08/2005	637,66	113,20	436,98	19,50	178,93	700,81	0,09	34,53	0,96	1,89	11,73	502,11	0,10	0,44	18,77	20,90	0,11
17/09/2005	207,52	40,78	382,27	33,00	130,26	325,62	0,07	25,54	0,85	1,64	9,36	344,71	36,70	0,44	10,13	8,61	0,11
27/09/2005	72,80	13,25	120,04	25,25	44,25	125,46	0,02	4,86	0,29	1,01	30,61	126,40	2,94	0,19	4,58	28,55	0,04
28/09/2005	64,70	15,34	121,76	36,19	37,26	116,04	0,03	9,13	0,27	0,90	37,78	114,77	3,73	0,14	3,11	6,35	0,03
20/10/2005	185,98	19,33	264,80	35,47	96,04	209,87	0,06	12,04	0,71	1,24	46,04	268,02	4,30	0,29	7,76	8,33	0,09

Table 4-c (continued): Chemical data for major and traces elements. PM10 at La Paz station. Date: 07/01/2005 - 20/10/2005

Table (4-c): La Paz (PM 10) ng/m^3

date	Ge	As	Rb	Sr	Y	Zr	Mo	Ag	Cd	Sn	Sb	Cs	Ba	Pb	Bi	U
13/01/2004	0,01	0,36	0,55	2,62	0,25	2,30	1,89	0,04	0,02	0,43	-	0,04	12,64	4,06	0,02	0,01
25/01/2004	0,01	0,15	0,36	1,59	0,10	0,57	3,73	0,03	0,02	0,19	-	0,03	9,98	1,61	0,01	0,004
18/02/2004	0,02	0,72	0,73	3,88	0,39	4,36	4,12	0,06	0,02	0,42	-	0,07	29,33	3,31	0,02	0,02
27/02/2004	0,01	0,19	0,35	1,77	0,10	0,51	0,68	0,04	0,02	0,45	-	0,03	11,57	1,95	0,01	0,01
25/03/2004	0,11	1,49	3,17	15,69	1,39	13,04	13,16	0,22	0,16	2,99	26,85	0,27	96,93	16,80	0,06	0,07
31/03/2004	0,01	0,20	0,33	2,23	0,11	0,66	4,45	0,05	0,02	0,35	-	0,03	23,82	2,68	0,02	0,005
13/04/2004	0,001	0,03	0,05	0,32	0,02	0,08	0,94	0,25	0,004	0,05	-	0,004	3,34	0,44	0,001	-
29/04/2004	0,01	0,72	0,19	1,16	0,06	0,40	1,57	0,37	0,02	0,24	-	0,02	14,15	1,97	0,01	0,002
30/04/2004	0,01	0,54	0,17	1,20	0,04	0,41	2,01	0,25	0,02	0,31	-	0,02	12,40	2,13	0,01	0,002
06/05/2004	0,01	0,34	0,19	1,16	0,05	0,37	0,43	0,23	0,02	0,37	-	0,02	12,17	2,49	0,01	0,002
07/05/2004	0,01	0,47	0,13	1,08	0,04	0,38	1,33	0,11	0,02	0,36	-	0,01	8,32	2,27	0,01	0,003
18/05/2004	0,01	0,33	0,15	1,02	0,05	0,32	0,88	0,29	0,02	0,37	-	0,01	10,12	2,09	0,01	0,001
21/05/2004	0,001	0,03	0,03	0,20	0,01	0,07	0,04	0,08	0,003	0,005	-	0,002	3,62	0,62	0,001	-
30/05/2004	0,005	0,29	0,12	0,89	0,04	0,30	0,95	0,14	0,02	0,20	-	0,01	14,99	1,96	0,01	0,001
31/05/2004	0,01	0,36	0,19	1,36	0,05	0,48	0,57	0,29	0,03	0,38	0,003	0,02	16,84	3,96	0,01	0,002
15/06/2004	0,11	5,09	3,14	20,58	0,97	10,71	17,46	0,33	0,38	4,99	5,87	0,28	199,57	46,44	0,20	0,09
20/06/2004	0,01	0,69	0,31	2,19	0,09	0,93	5,15	0,13	0,04	1,13	1,31	0,04	31,50	5,77	0,03	0,01
13/07/2004	0,01	0,22	0,11	0,94	0,03	0,67	0,39	0,02	0,03	0,58	0,08	0,01	23,65	3,84	0,01	0,002
16/07/2004	0,07	2,24	1,45	10,34	0,50	5,02	3,17	0,18	0,24	3,51	4,61	0,13	138,73	29,26	0,11	0,05
29/07/2004	0,38	2,71	1,47	11,37	0,48	6,41	6,27	0,18	0,21	2,58	3,47	0,12	128,15	19,39	0,09	0,06
03/08/2004	0,01	0,21	0,30	2,33	0,11	1,28	1,24	0,04	0,05	0,53	0,25	0,02	29,76	3,60	0,04	0,01
23/08/2004	0,07	2,07	2,22	15,72	0,56	8,11	11,40	0,25	0,27	3,48	4,29	0,22	173,47	21,59	0,10	0,07
26/08/2004	0,05	1,98	0,92	6,96	0,28	2,97	4,42	0,10	0,12	2,85	4,80	0,07	71,26	15,74	0,06	0,03
02/09/2004	0,02	1,20	0,55	3,65	0,16	1,83	1,98	0,13	0,05	0,15	82,30	0,05	36,24	5,59	0,04	0,02
18/09/2004	0,001	0,08	0,05	0,71	0,01	0,08	0,66	0,07	0,004	0,04	54,29	0,004	2,58	0,29	0,01	0,002
02/10/2004	0,01	0,31	0,29	1,83	0,05	0,57	0,34	0,08	0,01	0,23	67,90	0,03	8,77	1,69	0,03	0,01
12/10/2004	0,003	0,09	0,10	1,20	0,03	0,24	0,46	0,08	0,01	0,12	68,84	0,01	5,16	1,02	0,01	0,003

Table 4-c (continued): Chemical data for major and traces elements. PM10 at La Paz station. Date: 13/01/2004 - 12/10/2004.

Table (4-c): La Paz (PM 10) ng/m^3

date	Ge	As	Rb	Sr	Y	Zr	Mo	Ag	Cd	Sn	Sb	Cs	Ba	Pb	Bi	U
07/01/2005	0,005	0,12	0,31	1,49	0,08	0,38	3,25	0,02	0,02	0,14	-	0,02	8,17	1,13	0,01	0,002
31/01/2005	0,004	0,16	0,23	1,31	0,07	0,37	0,62	0,02	0,02	0,14	-	0,02	10,86	1,24	0,01	0,003
03/02/2005	0,01	0,26	0,57	2,86	0,11	0,90	1,57	0,04	0,02	0,21	-	0,04	9,97	2,51	0,01	0,01
12/02/2005	0,004	0,12	0,18	0,93	0,05	0,22	0,26	0,03	0,01	0,16	-	0,01	7,28	0,96	0,004	0,001
26/03/2005	0,003	0,06	0,17	0,83	0,04	0,22	0,16	0,02	0,001	0,18	-	0,01	4,60	0,63	0,002	0,001
30/03/2005	0,02	0,33	0,68	3,25	0,18	1,25	5,08	0,04	0,04	1,06	-	0,05	18,47	3,47	0,01	0,01
10/04/2005	0,003	0,06	0,12	0,59	0,03	0,18	0,49	0,19	0,005	0,22	-	0,01	5,26	0,52	0,004	0,0001
15/04/2005	0,03	0,28	0,14	1,36	0,05	0,46	0,91	0,26	0,02	0,38	-	0,01	14,18	2,54	0,02	0,003
29/04/2005	0,01	0,20	0,21	1,71	0,07	0,62	0,68	0,32	0,02	0,56	-	0,02	22,86	2,89	0,01	0,003
27/05/2005	0,11	2,30	1,32	14,58	0,55	6,34	4,08	2,13	0,35	4,77	4,57	0,17	129,28	38,15	0,16	0,06
07/06/2005	0,08	3,21	1,72	12,22	0,35	5,47	11,74	0,15	0,27	4,11	4,25	0,16	132,25	26,88	0,12	0,06
08/06/2005	0,05	5,50	0,97	6,69	0,21	3,36	5,89	0,07	0,16	3,12	3,62	0,09	76,73	16,05	0,08	0,03
22/06/2005	0,10	2,77	2,00	17,26	0,73	10,35	11,47	0,26	0,21	4,63	4,72	0,14	191,60	33,43	0,13	0,10
27/06/2005	0,01	0,17	0,09	0,76	0,04	0,78	0,59	0,01	0,02	0,28	-	0,01	15,96	2,15	0,01	0,002
09/07/2005	0,08	2,48	1,53	11,67	0,37	4,91	8,38	0,11	0,18	3,78	3,63	0,12	142,41	18,54	0,11	0,06
14/07/2005	0,02	0,49	0,48	4,05	0,16	1,41	0,80	0,04	0,07	0,96	1,48	0,04	58,40	11,47	0,03	0,01
27/07/2005	0,04	0,97	1,22	7,46	0,34	2,69	4,28	0,10	0,15	2,23	1,29	0,11	61,77	12,88	0,04	0,03
28/07/2005	0,07	2,24	1,45	11,63	1,53	31,39	7,55	0,23	0,26	3,65	3,75	0,14	81,40	23,87	0,11	0,05
02/08/2005	0,02	0,60	0,49	3,86	0,16	1,60	3,08	0,06	0,08	1,20	0,54	0,04	42,57	7,68	0,05	0,01
10/08/2005	0,07	2,39	1,65	11,86	0,59	5,68	8,85	0,11	0,19	4,13	5,43	0,19	75,82	20,39	0,13	0,06
18/08/2005	0,09	2,49	2,44	15,42	0,39	9,31	6,64	0,11	0,17	3,29	3,77	0,23	130,64	23,24	0,09	0,10
21/08/2005	0,01	0,51	0,42	3,70	0,11	1,22	3,19	0,04	0,03	2,47	0,45	0,03	38,25	3,68	0,02	0,02
17/09/2005	0,01	0,63	0,36	2,14	0,09	0,77	0,92	0,18	0,04	0,69	138,64	0,03	14,48	2,22	0,01	0,01
27/09/2005	0,004	0,16	0,14	1,11	0,03	0,29	0,87	0,06	0,01	0,10	45,58	0,01	4,80	1,06	0,02	0,004
28/09/2005	0,003	0,16	0,12	1,14	0,03	0,23	0,31	0,07	0,01	0,24	70,27	0,01	5,12	0,64	0,01	0,004
20/10/2005	0,01	0,28	0,33	2,14	0,07	0,52	2,36	0,08	0,02	0,17	53,62	0,03	8,27	1,54	0,01	0,01

Table 4-c (continued): Chemical data for major and traces elements. PM10 at La Paz station. Date: 07/01/2005 - 20/10/2005

Table 4-d: La Paz REEs (PM 10) ng/m^3

date	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Hf	W
13/01/2004	0,16	0,36	0,04	0,16	0,03	0,01	0,04	0,01	0,03	0,01	0,02	0,02	0,05	0,01
25/01/2004	0,10	0,23	0,03	0,10	0,02	0,01	0,02	0,003	0,02	0,004	0,01	0,01	0,0004	-
18/02/2004	0,21	0,49	0,05	0,21	0,04	0,01	0,05	0,01	0,04	0,01	0,02	0,02	0,08	0,03
27/02/2004	0,11	0,25	0,03	0,11	0,02	0,01	0,02	0,003	0,02	0,003	0,01	0,01	0,01	0,01
25/03/2004	0,89	1,96	0,23	0,90	0,19	0,06	0,20	0,03	0,17	0,03	0,10	0,09	0,25	0,53
31/03/2004	0,11	0,27	0,03	0,10	0,02	0,01	0,02	0,003	0,02	0,003	0,01	0,01	0,01	0,02
13/04/2004	0,02	0,04	0,004	0,01	0,003	0,001	0,003	0,0005	0,003	0,0004	0,001	0,001	-	-
29/04/2004	0,06	0,16	0,01	0,05	0,01	0,004	0,01	0,002	0,01	0,002	0,01	0,005	0,01	0,01
30/04/2004	0,05	0,14	0,01	0,05	0,01	0,004	0,01	0,001	0,01	0,001	0,004	0,004	0,01	0,01
06/05/2004	0,06	0,15	0,01	0,05	0,01	0,004	0,01	0,002	0,01	0,002	0,01	0,005	0,01	0,02
07/05/2004	0,05	0,17	0,01	0,05	0,01	0,003	0,01	0,001	0,01	0,001	0,004	0,004	0,005	0,01
18/05/2004	0,05	0,11	0,01	0,04	0,01	0,003	0,01	0,001	0,01	0,002	0,004	0,005	0,004	0,02
21/05/2004	0,01	0,03	0,00	0,01	0,002	0,001	0,002	0,0003	0,002	0,0003	0,001	0,001	-	-
30/05/2004	0,05	0,11	0,01	0,03	0,01	0,003	0,01	0,001	0,01	0,001	0,003	0,003	0,003	-
31/05/2004	0,06	0,15	0,01	0,05	0,01	0,004	0,01	0,002	0,01	0,002	0,01	0,01	0,01	0,06
15/06/2004	1,00	2,51	0,24	0,96	0,2	0,07	0,22	0,03	0,17	0,03	0,10	0,09	0,24	0,93
20/06/2004	0,15	0,32	0,03	0,11	0,02	0,01	0,02	0,02	0,003	0,01	0,001	0,01	0,02	0,04
13/07/2004	0,06	0,17	0,01	0,04	0,01	0,004	0,01	0,001	0,01	0,001	0,003	0,003	0,01	0,03
16/07/2004	0,57	1,45	0,13	0,51	0,10	0,04	0,12	0,02	0,09	0,02	0,05	0,05	0,12	0,50
29/07/2004	0,56	1,64	0,13	0,52	0,10	0,04	0,13	0,02	0,09	0,02	0,05	0,05	0,15	0,58
03/08/2004	0,12	0,32	0,03	0,09	0,02	0,01	0,02	0,003	0,02	0,003	0,01	0,01	0,03	0,47
23/08/2004	0,74	2,01	0,17	0,63	0,12	0,05	0,15	0,02	0,10	0,02	0,06	0,05	0,18	0,42
26/08/2004	0,35	0,89	0,08	0,30	0,06	0,02	0,08	0,01	0,05	0,01	0,03	0,03	0,07	0,24
02/09/2004	0,25	0,60	0,04	0,16	0,03	0,01	0,04	0,005	0,03	0,01	0,02	0,02	0,04	0,02
18/09/2004	0,02	0,03	0,003	0,01	0,002	0,001	0,002	0,0003	0,002	0,0002	0,001	0,001	0,001	0,00
02/10/2004	0,06	0,18	0,01	0,06	0,01	0,003	0,01	0,002	0,01	0,002	0,01	0,005	0,01	0,01
12/10/2004	0,03	0,08	0,01	0,03	0,01	0,002	0,01	0,001	0,00	0,001	0,003	0,003	0,00	0,01

Table 4-d: Chemical data for REEs elements. PM10 at La Paz station. Date: 13/01/2004 - 12/10/2004.

Table 4-d: La Paz REEs (PM 10) ng/m^3

date	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Hf	W
07/01/2005	0,09	0,19	0,02	0,08	0,02	0,005	0,02	0,002	0,01	0,003	0,01	0,01	0,004	-
31/01/2005	0,08	0,18	0,02	0,08	0,01	0,004	0,01	0,002	0,01	0,002	0,01	0,01	0,004	-
03/02/2005	0,13	0,37	0,03	0,12	0,03	0,01	0,03	0,003	0,02	0,004	0,01	0,01	0,02	-
12/02/2005	0,07	0,15	0,01	0,05	0,01	0,003	0,01	0,001	0,01	0,002	0,005	0,004	0,001	-
26/03/2005	0,05	0,11	0,01	0,05	0,01	0,003	0,01	0,001	0,01	0,001	0,004	0,004	0,001	0,0004
30/03/2005	0,16	0,38	0,04	0,16	0,04	0,01	0,04	0,01	0,03	0,01	0,02	0,02	0,03	0,12
10/04/2005	0,04	0,09	0,01	0,03	0,01	0,002	0,01	0,001	0,01	0,001	0,003	0,003	0,00005	-
15/04/2005	0,08	0,18	0,02	0,07	0,01	0,005	0,02	0,002	0,01	0,002	0,01	0,01	0,01	0,01
29/04/2005	0,11	0,23	0,02	0,10	0,02	0,01	0,02	0,002	0,01	0,002	0,01	0,01	0,01	0,02
27/05/2005	0,92	2,02	0,20	0,82	0,14	0,05	0,17	0,02	0,11	0,02	0,07	0,06	0,14	0,61
07/06/2005	0,56	1,63	0,12	0,45	0,09	0,04	0,12	0,01	0,07	0,01	0,04	0,04	0,13	0,47
08/06/2005	0,37	0,89	0,07	0,26	0,05	0,02	0,07	0,01	0,04	0,01	0,02	0,02	0,08	0,33
22/06/2005	0,88	2,31	0,19	0,79	0,16	0,06	0,19	0,02	0,13	0,03	0,08	0,07	0,24	1,14
27/06/2005	0,11	0,15	0,01	0,04	0,01	0,003	0,01	0,001	0,00	0,001	0,003	0,003	0,01	0,08
09/07/2005	0,64	1,54	0,13	0,47	0,09	0,04	0,11	0,01	0,07	0,01	0,041	0,04	0,12	0,14
14/07/2005	0,22	0,52	0,05	0,19	0,03	0,02	0,04	0,01	0,03	0,01	0,017	0,01	0,03	0,25
27/07/2005	0,49	0,92	0,10	0,37	0,08	0,02	0,09	0,01	0,06	0,01	0,036	0,03	0,06	0,56
28/07/2005	0,59	1,40	0,13	0,51	0,11	0,04	0,12	0,08	0,02	0,05	0,003	0,04	0,60	0,46
02/08/2005	0,21	0,54	0,05	0,17	0,03	0,01	0,04	0,005	0,03	0,01	0,016	0,01	0,03	0,14
10/08/2005	0,67	1,48	0,16	0,63	0,14	0,04	0,15	0,12	0,02	0,07	0,004	0,06	0,19	0,46
18/08/2005	0,66	2,79	0,14	0,53	0,10	0,04	0,12	0,01	0,08	0,02	0,049	0,04	0,21	0,94
21/08/2005	0,19	0,40	0,04	0,13	0,03	0,01	0,03	0,004	0,02	0,004	0,012	0,01	0,02	0,07
17/09/2005	0,11	0,32	0,02	0,09	0,02	0,01	0,02	0,003	0,02	0,003	0,009	0,01	0,02	0,02
27/09/2005	0,05	0,15	0,01	0,04	0,01	0,002	0,01	0,001	0,01	0,001	0,004	0,004	0,01	0,01
28/09/2005	0,05	0,11	0,01	0,03	0,01	0,002	0,01	0,001	0,01	0,001	0,004	0,004	0,01	0,06
10/20/200	0,09	0,27	0,02	0,08	0,02	0,005	0,02	0,002	0,01	0,003	0,008	0,01	0,01	0,03

Table 4-d (continued): Chemical data for REEs elements. PM10 at La Paz station. Date: 07/01/2005 - 10/20/2005.

Table (4-e): Las Condes (PM 2.5) ng/m^3

date	Na	Mg	Al	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
13/01/2004	42,86	4,11	14,83	-	9,10	8,39	-	1,08	0,11	-	0,59	15,87	-	-	1,56	-	0,01
25/01/2004	163,17	14,72	110,91	1,97	37,52	142,28	0,01	2,71	0,19	-	0,88	37,29	-	-	2,30	-	0,02
03/02/2004	520,63	54,19	98,45	5,95	345,73	592,80	0,02	7,27	0,65	0,19	4,19	100,74	-	-	7,45	5,09	0,04
27/02/2004	97,54	10,50	57,47	2,34	41,61	108,26	0,02	3,05	0,26	-	2,01	45,98	-	-	2,26	1,06	0,02
23/03/2004	179,01	28,60	118,36	5,34	204,18	366,41	0,03	7,23	0,42	0,76	4,87	106,93	-	-	7,40	11,67	0,05
31/03/2004	121,29	4,01	12,89	2,06	18,40	85,95	-	1,49	0,10	-	1,37	29,40	-	-	1,82	-	0,01
29/04/2004	8,97	-	6,77	-	36,53	-	-	0,61	0,07	-	1,72	22,64	-	-	2,55	-	0,02
30/04/2004	9,82	0,42	6,26	-	33,62	-	-	0,90	0,08	-	1,83	31,35	-	-	3,28	-	0,02
10/05/2004	352,81	28,11	113,71	29,61	521,16	699,76	0,02	18,54	0,70	5,63	20,00	323,08	0,13	3,04	37,01	55,66	0,20
17/05/2004	13,27	2,40	16,65	-	45,43	-	-	1,42	0,10	-	2,13	44,23	-	-	3,78	-	0,02
19/05/2004	413,47	47,41	228,69	44,12	809,35	673,55	0,04	329,35	3,77	496,66	62,98	2309,78	6,88	734,39	54,28	169,82	0,41
22/05/2004	-	-	-	-	-	-	-	0,03	0,004	-	0,17	5,23	-	-	0,68	-	0,002
31/05/2004	-	-	-	-	-	-	-	0,18	0,003	-	0,17	5,90	-	-	0,29	-	0,002
20/06/2004	250,60	31,94	22,71	3,03	289,79	425,53	0,01	1,26	0,06	1,15	1,28	51,07	-	0,80	5,62	27,37	0,01
24/06/2004	129,47	36,44	163,95	19,08	403,80	200,96	0,03	14,75	0,65	11,36	42,08	548,43	0,37	3,42	55,31	167,65	0,38
12/07/2004	105,12	11,93	63,94	13,23	467,07	203,91	0,01	8,17	0,86	13,38	18,42	309,63	0,35	12,48	32,17	100,37	0,22
16/07/2004	77,69	22,74	78,79	9,65	403,00	102,37	0,02	9,64	0,31	12,44	12,13	295,10	0,25	10,55	20,88	36,73	0,13
03/08/2004	37,97	10,59	46,97	3,44	66,97	13,64	0,00	1,85	0,09	0,42	3,12	69,78	-	-	4,84	6,58	0,04
25/08/2004	217,36	51,66	190,09	16,96	347,10	179,76	0,03	10,88	0,84	2,56	18,13	291,66	0,11	0,65	33,62	52,05	0,20
27/08/2004	133,61	31,66	129,43	17,20	310,20	146,49	0,03	12,29	0,63	2,85	22,48	356,33	0,08	0,59	36,76	70,11	0,21
21/07/2004	30,67	8,38	56,61	2,12	107,10	69,72	-	2,20	0,10	1,12	3,99	80,29	0,06	3,64	5,21	14,55	0,04
02/09/2004	33,69	7,39	33,85	15,05	53,42	56,83	0,02	1,45	0,14	1,11	3,35	61,71	26,77	0,33	6,73	19,15	0,03
14/09/2004	40,12	6,16	23,87	13,56	44,29	36,11	0,02	11,43	0,17	1,12	2,52	43,20	27,12	0,32	3,55	11,38	0,03
02/10/2004	16,70	2,65	14,81	8,31	30,13	16,59	0,02	0,30	0,06	0,90	0,96	18,19	24,39	0,31	2,11	4,33	0,01
04/10/2004	22,73	3,99	22,32	29,86	37,88	27,36	0,01	0,15	0,08	0,82	41,92	24,78	4,27	0,13	3,38	4,97	0,02
12/10/2004	59,11	6,66	12,82	53,91	17,51	21,14	0,02	0,58	0,04	0,91	61,73	18,22	6,36	0,65	2,11	2,77	0,01

Table 4-e: Chemical data for major and traces elements. PM2,5 at Las Condes station. Date: 13/01/2004 - 12/10/2004.

Table (4-e): Las Condes (PM 2.5) ng/m^3																	
date	**Na**	**Mg**	**Al**	**P**	**K**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**
07/01/2005	266,20	25,59	83,35	1,05	238,46	241,94	0,01	5,26	0,22	-	3,24	76,86	-	-	2,72	-	0,03
03/02/2005	1707,68	307,04	198,04	13,23	1145,97	3410,40	0,04	15,45	0,77	12,82	15,07	187,14	0,20	11,31	22,09	26,24	0,06
06/02/2005	216,36	20,30	39,88	-	244,65	-	0,003	10,96	0,36	-	0,86	34,76	-	-	1,73	-	0,01
30/03/2005	150,10	24,81	118,89	8,97	227,48	143,44	0,02	9,05	0,76	1,00	9,84	171,89	0,003	0,08	12,72	23,21	0,08
02/04/2005	11,36	0,22	4,78	-	7,95	-	-	0,53	0,08	-	0,36	13,54	-	-	1,43	-	0,004
23/04/2005	13,01	3,10	24,68	-	99,40	-	-	1,77	0,19	-	1,57	34,63	-	-	2,75	-	0,02
27/04/2005	9,21	0,50	7,92	-	44,70	-	-	0,96	0,19	-	1,92	28,47	-	-	3,22	0,73	0,02
02/05/2005	10,59	-	2,87	-	50,18	-	-	0,94	0,22	-	2,09	31,02	-	-	4,93	-	0,02
23/05/2005	-	-	1,62	-	-	-	-	-	0,01	-	-	0,74	-	-	0,43	-	0,001
31/05/2005	13,99	0,88	11,56	-	29,17	-	-	1,44	0,10	0,13	3,46	55,93	-	-	4,84	4,10	0,03
25/06/2005	73,95	18,17	65,09	21,84	251,79	212,32	0,02	7,82	1,15	6,05	20,54	298,34	0,12	0,81	36,63	88,01	0,25
27/06/2005	101,08	13,96	16,33	1,84	125,18	132,44	0,002	1,11	0,13	1,30	0,96	35,41	-	-	3,69	5,68	0,02
02/07/2005	69,60	9,24	58,96	5,94	132,94	-	0,005	4,86	0,20	16,80	3,21	136,66	0,28	21,98	6,18	12,02	0,02
28/07/2005	246,89	69,41	243,27	44,91	537,22	327,92	-	29,67	2,28	9,30	40,34	699,00	0,58	4,01	72,23	187,65	0,41
29/07/2005	204,47	52,37	192,42	34,42	613,17	327,59	0,05	17,57	3,19	10,25	32,08	551,02	0,30	2,17	67,44	131,79	0,36
10/08/2005	592,37	444,32	2483,09	77,77	610,32	2494,96	-	207,03	5,21	9,91	59,94	2505,84	1,12	2,93	67,54	85,67	0,65
12/08/2005	148,58	37,39	180,67	37,25	360,77	235,46	0,04	22,88	1,47	6,71	29,64	517,28	0,16	2,37	52,48	77,95	0,30
16/08/2005	41,25	5,52	22,05	3,64	60,31	-	0,001	0,91	0,09	0,18	1,44	36,59	-	-	5,49	5,00	0,01
03/09/2005	65,44	3,54	12,95	0,86	25,04	96,13	-	1,63	0,23	0,17	1,50	33,28	-	-	2,93	-	0,02
05/09/2005	29,00	4,31	19,64	11,12	67,01	29,66	0,02	0,82	0,08	1,47	2,79	57,80	26,55	0,29	4,29	13,91	0,03
15/09/2005	10,16	1,24	7,21	13,19	10,56	10,82	0,01	0,42	0,09	0,86	1,03	15,32	26,51	0,14	1,00	3,05	0,01
17/09/2005	40,70	5,20	138,13	14,38	59,69	28,74	0,01	1,15	0,14	1,12	1,09	31,66	25,58	0,55	4,60	7,25	0,03
08/10/2005	25,67	3,05	12,43	28,16	23,87	19,19	0,02	0,56	0,09	0,79	38,36	25,96	3,86	0,19	4,05	6,44	0,01
18/10/2005	78,64	8,75	47,01	4,26	47,26	57,87	0,01	3,48	0,19	-	3,50	73,64	-	-	5,20	3,37	0,04
24/10/2005	39,16	3,74	15,47	12,30	41,83	26,60	0,01	0,84	0,10	0,86	2,62	31,53	24,72	0,28	2,07	7,11	0,02

Table 4-e (continued): Chemical data for major and traces elements. PM2,5 at Las Condes station. Date:07/01/2005 - 24/10/2005.

Table (4-e): Las Condes (PM 2.5) ng/m^3

date	Ge	As	Rb	Sr	Y	Zr	Mo	Ag	Cd	Sn	Sb	Cs	Ba	Pb	Bi	U
13/01/2004	0,0002	0,30	0,03	0,07	0,005	0,01	0,10	0,02	0,01	0,16	-	0,002	0,68	0,68	0,005	-
25/01/2004	0,001	0,40	0,10	0,24	0,01	0,09	0,14	0,02	0,02	0,58	-	0,004	1,38	1,46	0,01	-
03/02/2004	0,01	1,08	0,41	0,89	0,03	0,20	0,77	0,15	0,11	0,99	-	0,01	4,44	3,68	0,03	-
27/02/2004	0,003	0,43	0,09	0,24	0,02	0,15	0,49	0,05	0,04	0,34	-	0,004	1,87	2,41	0,02	0,0002
23/03/2004	0,01	3,33	0,44	0,59	0,03	0,24	0,87	0,06	0,08	1,36	1,17	0,01	4,73	4,26	0,04	-
31/03/2004	0,003	0,28	0,04	0,14	0,01	0,12	0,44	0,09	0,03	0,94	-	0,001	1,73	1,66	0,01	-
29/04/2004	0,01	1,65	0,08	0,04	0,001	0,02	0,42	0,32	0,05	0,46	-	0,002	1,31	2,37	0,02	-
30/04/2004	0,01	2,18	0,09	0,06	0,002	0,04	0,45	0,27	0,06	0,39	-	0,003	1,79	3,15	0,02	-
10/05/2004	0,07	8,92	1,02	1,31	0,03	0,70	2,40	0,37	0,72	7,56	3,03	0,04	20,33	29,51	0,25	0,001
17/05/2004	0,01	1,19	0,11	0,12	0,01	0,07	0,31	0,42	0,06	0,58	-	0,01	2,96	2,24	0,07	-
19/05/2004	0,15	12,75	1,52	2,48	0,05	1,01	18,14	0,45	1,00	7,32	18,62	0,07	24,61	46,90	0,49	0,004
22/05/2004	0,0002	0,14	0,02	-	-	-	0,03	0,12	0,01	0,02	-	0,0004	0,61	0,53	0,002	-
31/05/2004	-	0,08	0,01	-	-	-	-	0,15	0,01	0,05	-	-	0,49	0,37	0,001	-
20/06/2004	0,01	1,76	0,38	1,08	0,01	0,81	0,22	0,01	0,07	0,63	-	0,01	4,10	4,28	0,02	0,03
24/06/2004	0,16	12,89	0,92	1,53	0,04	1,28	5,62	0,30	1,27	11,00	5,19	0,06	27,14	73,78	0,33	0,01
12/07/2004	0,09	15,55	0,92	0,79	0,02	0,61	2,36	0,55	1,03	9,53	4,97	0,03	15,30	38,16	0,38	0,004
16/07/2004	0,04	9,92	0,81	0,76	0,03	0,62	0,90	0,12	0,34	3,08	4,89	0,04	18,85	22,95	0,16	0,003
03/08/2004	0,01	0,74	0,13	0,24	0,01	0,23	0,15	0,02	0,12	0,39	-	0,005	3,56	3,64	0,02	0,001
25/08/2004	0,06	14,62	0,70	0,89	0,08	1,57	3,58	0,15	0,36	4,13	0,93	0,03	9,61	16,99	0,17	0,04
27/08/2004	0,08	8,39	0,62	1,01	0,52	8,49	3,04	0,22	0,62	5,79	2,31	0,03	17,46	32,13	0,18	0,01
21/07/2004	0,01	1,75	0,21	0,31	0,01	0,18	0,48	0,07	0,12	0,46	1,07	0,01	4,51	5,66	0,04	-
02/09/2004	0,01	2,74	0,09	0,24	0,01	0,14	0,80	0,10	0,10	0,33	92,16	0,005	3,28	3,68	0,03	0,01
14/09/2004	0,01	2,37	0,09	0,21	0,01	0,15	0,62	0,08	0,09	0,56	103,61	0,004	5,52	3,55	0,03	0,001
02/10/2004	0,002	0,74	0,07	0,08	0,004	0,04	0,18	0,06	0,03	0,13	70,31	0,002	0,83	1,41	0,01	0,003
04/10/2004	0,002	1,24	0,08	0,72	0,01	0,04	0,27	0,09	0,04	0,04	37,78	0,003	1,34	1,71	0,03	0,002
12/10/2004	0,003	0,28	0,03	0,93	0,00	0,06	0,09	0,10	0,03	0,14	101,55	0,001	1,16	0,92	0,01	0,0004

Table 4-e (continued): Chemical data for major and traces elements. PM2,5 at Las Condes station. Date: 13/01/2005 - 12/10/2004.

Table (4-e): Las Condes (PM 2.5) ng/m^3																
date	**Ge**	**As**	**Rb**	**Sr**	**Y**	**Zr**	**Mo**	**Ag**	**Cd**	**Sn**	**Sb**	**Cs**	**Ba**	**Pb**	**Bi**	**U**
07/01/2005	0,005	0,40	0,37	0,51	0,02	0,13	0,70	0,05	0,06	0,55	-	0,01	2,65	2,54	0,01	-
03/02/2005	0,01	1,61	1,04	8,16	0,05	0,35	0,58	0,08	0,10	3,40	0,33	0,02	7,24	3,89	0,11	0,01
06/02/2005	0,004	0,68	0,31	0,28	0,01	0,06	0,31	0,05	0,04	0,50	-	0,01	4,90	1,24	0,02	-
30/03/2005	0,02	1,56	0,52	0,67	0,08	1,07	3,00	0,06	0,18	2,48	0,27	0,02	6,97	10,09	0,06	-
02/04/2005	0,00	0,49	0,04	0,01	0,001	0,02	0,09	0,37	0,07	0,10	-	0,000	0,79	1,61	0,01	-
23/04/2005	0,004	1,07	0,17	0,09	0,01	0,06	0,24	-	0,04	0,37	-	0,004	1,61	1,49	0,02	-
27/04/2005	0,01	0,57	0,08	0,04	0,002	0,03	0,58	0,39	0,05	0,65	-	0,002	1,45	1,96	0,02	-
02/05/2005	0,01	1,25	0,09	0,02	0,001	0,04	0,34	0,12	0,04	0,80	-	0,003	0,63	1,51	0,02	-
23/05/2005	0,0001	0,27	0,004	-	-	-	-	0,04	0,01	0,03	-	-	0,25	0,40	0,01	-
31/05/2005	0,01	1,70	0,09	0,10	0,004	0,10	0,44	0,46	0,07	0,58	-	0,01	3,11	5,23	0,04	-
25/06/2005	0,08	13,48	0,63	0,75	0,03	0,78	5,75	0,19	0,55	5,78	3,39	0,04	15,55	53,83	0,28	0,01
27/06/2005	0,01	1,59	0,24	0,44	0,01	0,38	0,26	0,02	0,06	0,49	-	0,01	2,89	2,77	0,02	0,003
02/07/2005	0,01	3,85	0,29	0,24	0,01	0,43	0,62	0,02	0,54	1,28	0,73	0,01	6,08	4,51	0,10	0,001
28/07/2005	0,20	10,63	1,03	2,00	0,09	1,80	5,14	0,32	1,20	14,41	10,24	0,07	37,89	76,19	0,22	0,01
29/07/2005	0,15	15,39	1,32	1,67	0,06	1,33	8,55	0,39	1,16	12,76	7,25	0,07	31,56	66,01	0,31	0,01
10/08/2005	0,09	2,97	2,05	14,73	0,73	7,05	10,99	0,13	0,24	5,14	6,74	0,23	94,17	25,32	0,17	0,08
12/08/2005	0,13	10,81	0,72	1,54	0,05	1,64	6,94	0,25	0,75	18,26	5,89	0,04	28,34	38,35	0,29	0,03
16/08/2005	0,01	1,64	0,12	0,10	0,005	0,14	0,26	0,01	0,06	0,77	-	0,004	2,91	2,45	0,02	0,01
03/09/2005	0,01	0,56	0,06	0,13	0,02	0,40	0,56	0,04	0,04	1,27	-	0,003	1,69	2,08	0,02	-
05/09/2005	0,01	0,91	0,13	0,17	0,01	0,14	1,30	0,12	0,10	0,23	91,97	0,01	4,29	0,20	0,30	0,50
15/09/2005	0,002	0,23	0,02	0,03	0,001	0,03	0,13	0,07	0,02	0,28	110,71	0,001	0,59	1,05	0,005	0,001
17/09/2005	0,01	3,08	0,12	0,16	0,005	0,10	0,53	0,09	0,06	0,48	107,86	0,006	2,31	2,84	0,03	0,01
08/10/2005	0,004	2,76	0,05	0,67	0,004	0,06	0,64	0,12	0,04	0,19	50,80	0,003	2,42	3,16	0,04	0,003
18/10/2005	0,01	3,12	0,14	0,28	0,04	0,50	1,36	0,04	0,07	0,30	-	0,006	3,73	4,34	0,08	-
24/10/2005	0,004	0,38	0,05	0,09	0,003	0,06	0,54	0,07	0,04	0,20	102,44	0,002	0,77	1,05	0,02	0,002

Table 4-e (continued): Chemical data for major and traces elements. PM2,5 at Las Condes station. Date: 07/01/2005 - 24/10/2005.

Table (4-f): Las Condes REEs (PM 2.5) ng/m^3

date	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Hf	W
13/01/2004	0,01	0,01	0,001	0,0004	0,001	0,0001	0,0004	0,0001	0,001	0,0001	0,0003	0,0003	-	-
25/01/2004	0,02	0,04	0,004	0,01	0,003	0,0005	0,003	0,0004	0,002	0,0004	0,001	0,001	-	-
03/02/2004	0,09	0,10	0,01	0,03	0,01	0,002	0,01	0,001	0,005	0,001	0,003	0,003	0,0001	0,02
27/02/2004	0,02	0,04	0,004	0,01	0,002	0,001	0,002	0,0004	0,002	0,0003	0,001	0,001	-	-
23/03/2004	0,04	0,10	0,01	0,02	0,01	0,002	0,01	0,001	0,004	0,001	0,003	0,002	-	0,01
31/03/2004	0,01	0,02	0,002	0,001	0,0004	0,0002	0,001	0,0001	0,001	0,00004	0,0004	0,0002	-	0,08
29/04/2004	0,01	0,01	0,001	-	0,001	0,00001	0,0001	-	0,0001	-	-	0,00001	-	-
30/04/2004	0,01	0,02	0,001	-	0,0002	0,0001	0,0003	0,00002	0,0003	-	-	0,0001	-	0,0001
10/05/2004	0,10	0,27	0,02	0,04	0,01	0,003	0,01	0,001	0,005	0,001	0,003	0,003	0,01	0,063
17/05/2004	0,01	0,03	0,002	0,002	0,001	0,0003	0,001	0,0001	0,001	0,0001	0,0002	0,0004	-	-
19/05/2004	0,13	0,35	0,03	0,07	0,01	0,005	0,01	0,002	0,01	0,002	0,01	0,01	0,02	0,41
22/05/2004	0,001	0,001	0,0001	-	-	-	-	-	-	-	-	-	-	-
31/05/2004	0,0005	-	0,0000	-	-	-	-	-	-	-	-	-	-	-
20/06/2004	0,02	0,06	0,004	0,01	0,002	0,001	0,002	0,0003	0,001	0,0002	0,001	0,001	0,02	0,01
24/06/2004	0,12	0,33	0,02	0,06	0,01	0,006	0,01	0,001	0,01	0,001	0,004	0,004	0,03	0,35
12/07/2004	0,17	0,26	0,02	0,05	0,003	0,003	0,02	0,001	0,004	0,001	0,002	0,002	0,01	0,35
16/07/2004	0,08	0,23	0,01	0,04	0,003	0,004	0,01	0,001	0,005	0,001	0,003	0,002	0,01	0,07
03/08/2004	0,01	0,04	0,003	0,005	0,001	0,001	0,001	0,0001	0,001	0,0002	0,0004	0,001	0,0003	0,05
25/08/2004	0,17	0,22	0,02	0,06	0,01	0,003	0,03	0,001	0,01	0,001	0,004	0,004	0,02	0,12
27/08/2004	0,15	0,28	0,02	0,05	0,01	0,004	0,02	0,001	0,01	0,001	0,004	0,004	0,14	0,06
21/07/2004	0,03	0,09	0,01	0,04	0,002	0,001	0,003	0,0003	0,001	0,0002	0,001	0,001	0,003	0,01
02/09/2004	0,02	0,04	0,003	0,01	0,002	0,001	0,003	0,0002	0,001	0,0003	0,001	0,001	0,002	0,02
14/09/2004	0,03	0,03	0,003	0,01	0,001	0,001	0,003	0,0002	0,001	0,0002	0,001	0,001	0,003	0,06
02/10/2004	0,01	0,02	0,002	0,01	0,001	0,0001	0,001	0,0001	0,001	0,0001	0,0003	0,0004	0,0004	0,00
04/10/2004	0,01	0,03	0,002	0,01	0,001	0,0004	0,001	0,0002	0,001	0,0002	0,001	0,001	0,0002	0,001
12/10/2004	0,01	0,02	0,001	0,003	0,0005	0,0003	0,001	0,0001	0,0004	0,0001	0,0002	0,0002	0,001	0,002

Table 4-f: Chemical data for REEs elements. PM2,5 at La Paz station. Date: 13/01/2004 - 12/10/2004.

Table (4-f): Las Condes REEs (PM 2.5) ng/m^3

DATE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Hf	W
07/01/2005	0,04	0,06	0,01	0,02	0,005	0,001	0,01	0,001	0,004	0,001	0,002	0,002	-	0,0004
03/02/2005	0,08	0,13	0,01	0,04	0,01	0,003	0,01	0,001	0,01	0,001	0,005	0,004	0,003	0,02
06/02/2005	0,04	0,04	0,005	0,01	0,002	0,001	0,01	0,0003	0,002	0,0004	0,001	0,002	0,0001	-
30/03/2005	0,07	0,13	0,01	0,04	0,01	0,002	0,01	0,001	0,01	0,001	0,004	0,0030	0,02	0,003
02/04/2005	0,01	0,01	0,001	-	0,0001	-	0,001	-	0,0002	-	-	0,0001	-	-
23/04/2005	0,01	0,02	0,002	0,005	0,001	0,0003	0,001	0,0002	0,001	0,0001	0,0004	0,001	-	-
27/04/2005	0,01	0,01	0,001	0,0003	0,001	0,0001	0,0004	-	0,0003	-	-	0,0001	-	-
02/05/2005	0,01	0,01	0,001	0,0002	0,0004	-	0,0004	0,00001	0,0002	-	-	0,0001	-	-
23/05/2005	-	0,0004	-	0,001	-	-	-	-	-	-	-	-	-	-
31/05/2005	0,01	0,03	0,002	0,0003	0,0004	0,0002	0,0003	0,00002	0,0005	-	0,0001	0,0002	-	0,01
25/06/2005	0,15	0,25	0,02	0,05	0,01	0,003	0,01	0,001	0,01	0,001	0,003	0,003	0,02	0,06
27/06/2005	0,02	0,04	0,002	0,002	0,001	0,001	0,001	0,0002	0,0004	0,0002	0,001	0,001	0,003	0,07
02/07/2005	0,03	0,09	0,004	0,01	-	0,001	0,002	0,0002	0,001	0,0002	0,001	0,0004	0,01	0,12
28/07/2005	0,25	0,43	0,03	0,11	0,02	0,01	0,03	0,01	0,002	0,01	0,0004	0,01	0,04	0,70
29/07/2005	0,28	0,44	0,03	0,10	0,01	0,01	0,03	0,002	0,01	0,002	0,01	0,01	0,03	0,28
10/08/2005	0,83	1,84	0,20	0,78	0,17	0,05	0,18	0,14	0,03	0,1	0,005	0,1	0,24	0,58
12/08/2005	0,20	0,36	0,03	0,07	0,01	0,005	0,02	0,002	0,01	0,002	0,01	0,005	0,03	0,33
16/08/2005	0,02	0,03	0,002	0,0001	0,001	0,0004	0,001	0,0001	0,0004	0,0001	0,0004	0,0004	-	0,02
03/09/2005	0,02	0,03	0,002	0,002	0,001	0,0003	0,001	0,0001	0,001	0,0001	0,0003	0,0002	0,005	0,07
05/09/2005	0,03	0,05	0,003	0,009	0,001	0,001	0,002	0,0002	0,001	0,0002	0,001	0,0005	0,002	0,01
15/09/2005	0,01	0,01	0,001	0,001	0,0001	0,0001	0,0004	0,00003	0,0002	0,00004	0,00002	0,0001	0,0004	0,12
17/09/2005	0,02	0,04	0,002	0,01	0,001	0,0004	0,001	0,0002	0,001	0,0001	0,0005	0,001	0,003	0,01
08/10/2005	0,02	0,03	0,002	0,01	0,001	0,001	0,001	0,0001	0,001	0,0001	0,0004	0,0004	0,001	0,02
18/10/2005	0,03	0,06	0,005	0,01	0,003	0,001	0,004	0,0004	0,002	0,0004	0,002	0,001	0,005	-
24/10/2005	0,02	0,02	0,001	0,004	0,001	0,0002	0,001	0,0001	0,001	0,0001	0,0003	0,0003	0,001	0,01

Table 4-f (continued): Chemical data for REEs elements. PM2,5 at La Paz station. Date: 07/01/2005 - 24/10/2005.

Table (4-g): Las Condes (PM 10) ng/m^3

date	Na	Mg	Al	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
13/01/2004	537,58	150,78	492,74	13,37	180,99	1394,06	0,11	30,78	0,91	4,48	12,05	341,99	0,17	3,25	10,79	5,41	0,11
25/01/2004	257,80	62,65	353,36	7,16	83,32	231,29	0,08	20,65	0,63	-	6,28	219,31	0,06	-	3,20	-	0,08
03/02/2004	293,25	46,79	306,95	7,02	131,93	367,88	0,07	24,71	0,77	0,06	7,83	261,63	0,06	-	4,26	8,12	0,09
27/02/2004	201,42	69,24	426,97	11,08	126,32	718,11	0,09	25,18	0,73	0,50	8,03	283,75	0,06	-	4,28	1,67	0,10
23/03/2004	104,14	32,17	289,51	3,30	65,34	208,97	0,05	21,54	0,55	-	5,83	219,11	0,03	-	4,60	-	0,07
31/03/2004	20,19	4,70	34,24	-	-	26,63	0,002	2,67	0,08	-	0,75	36,32	-	-	0,81	-	0,01
22/04/2004	12,15	6,38	50,23	-	-	11,65	0,003	3,07	0,08	-	0,93	44,41	-	-	1,13	-	0,01
29/04/2004	50,07	20,86	130,13	-	23,86	98,05	0,02	8,60	0,23	0,01	2,74	114,14	-	-	3,94	-	0,03
30/04/2004	52,34	28,16	190,36	-	34,61	154,34	0,04	13,31	0,32	0,16	3,84	164,32	-	-	5,33	-	0,04
10/05/2004	82,26	25,11	186,91	2,03	89,11	212,71	0,03	13,87	0,34	0,07	4,25	178,93	-	-	5,59	5,56	0,05
17/05/2004	81,85	55,48	390,14	2,52	76,00	313,02	0,08	23,29	0,60	0,16	7,64	306,62	0,06	-	8,00	-	0,09
19/05/2004	77,20	22,64	222,35	2,48	71,48	176,24	0,04	17,22	0,42	0,11	5,15	198,13	0,02	-	6,23	3,00	0,06
22/05/2004	10,87	5,11	38,25	-	-	-	0,001	2,88	0,07	-	0,75	35,42	-	-	1,00	-	0,01
20/06/2004	95,04	47,84	240,93	9,75	120,61	522,28	0,04	16,13	0,45	0,59	5,14	258,66	0,06	0,25	8,02	6,98	0,05
12/07/2004	322,42	113,12	655,70	31,97	273,04	1017,48	0,16	80,47	2,08	4,11	26,77	1105,57	0,40	1,04	36,31	45,26	0,26
16/07/2004	347,19	305,28	1661,94	37,27	348,56	1461,70	0,40	127,99	2,97	3,78	34,87	1636,43	0,58	0,96	41,97	39,14	0,38
21/07/2004	81,08	54,52	281,21	4,37	60,93	326,42	0,05	19,84	0,50	0,73	5,80	264,42	0,08	0,23	6,56	7,00	0,06
03/08/2004	3797,86	1236,90	177,36	7,06	582,54	11176,05	0,02	12,73	0,49	15,88	6,53	217,89	0,34	16,91	39,65	42,11	0,04
25/08/2004	281,67	69,72	461,21	10,34	149,99	598,41	0,10	38,24	1,07	0,92	11,66	444,40	0,18	-	11,67	6,38	0,13
27/08/2004	41,82	18,04	133,11	0,05	19,24	137,20	0,02	9,77	0,22	-	2,70	118,05	-	-	2,68	-	0,03
02/09/2004	110,93	45,49	388,33	15,66	98,08	379,94	0,09	17,97	0,72	1,31	8,70	332,14	22,23	0,61	8,75	9,81	0,10
07/09/2004	34,09	9,38	56,46	12,86	18,28	66,88	0,02	3,55	0,15	1,60	1,50	60,37	26,28	0,19	1,88	3,76	0,01
14/09/2004	135,46	13,37	169,13	15,43	86,37	167,31	0,04	14,32	0,51	1,12	5,42	197,29	21,42	0,31	5,95	12,50	0,06
02/10/2004	94,12	25,34	262,39	10,86	74,21	208,79	0,05	9,85	0,53	0,90	6,13	221,54	22,65	0,37	6,96	5,55	0,07

Table 4-g: Chemical data for major and traces elements. PM10 at Las Condes station. Date: 13/01/2004 - 02/10/2004.

Table (4-g): Las Condes (PM 10) ng/m^3

date	Na	Mg	Al	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
04/10/2004	106,33	27,23	310,04	37,87	99,48	287,99	0,07	14,84	0,68	1,08	46,50	299,90	4,23	0,28	7,06	7,37	0,10
12/10/2004	122,56	18,13	90,38	40,37	38,03	96,50	0,03	4,86	0,21	0,96	45,82	87,41	4,77	0,20	2,57	5,04	0,03
07/01/2005	408,41	97,13	539,81	8,44	172,81	689,18	0,11	31,27	0,92	0,59	10,22	349,31	0,13	-	5,07	3,13	0,12
03/02/2005	623,76	140,67	703,96	15,98	227,81	685,95	0,15	43,48	1,16	0,26	12,34	442,96	0,12	-	8,64	4,39	0,15
06/02/2005	343,02	67,41	351,28	5,64	128,35	465,98	0,07	20,67	0,63	-	6,28	222,77	0,01	-	3,68	-	0,08
09/03/2005	101,01	20,92	140,03	4,05	58,33	278,87	0,03	13,76	0,44	0,35	4,37	178,88	0,09	-	5,11	2,09	0,05
09/03/2005	35,07	10,03	36,66	8,96	20,70	32,84	0,01	1,76	0,06	0,75	0,84	39,20	18,07	0,91	2,16	3,58	0,01
30/03/2005	397,52	169,60	1132,89	24,58	291,79	993,87	0,24	80,43	1,87	1,45	20,93	758,69	0,28	0,16	14,47	14,02	0,24
02/04/2005	44,42	18,89	130,81	-	17,94	49,57	0,02	7,96	0,22	-	2,28	91,51	-	-	2,28	-	0,03
23/04/2005	51,97	33,15	237,77	0,91	50,09	148,39	0,05	15,39	0,41	-	4,50	172,91	-	-	4,39	-	0,05
27/04/2005	600,74	281,45	1782,35	49,47	460,80	1602,55	0,38	123,77	3,40	5,01	35,92	1427,70	0,58	1,39	43,75	39,20	0,41
23/05/2005	155,88	35,56	215,84	6,98	71,78	127,84	0,05	0,01	0,47	0,05	3,80	182,82	0,00	0,00	7,38	1,88	0,05
31/05/2005	622,41	328,74	2079,98	60,00	493,57	2032,59	0,45	480,95	4,20	17,29	44,67	1970,94	3,72	11,45	59,87	67,96	0,46
07/06/2005	522,49	191,39	1357,91	43,91	420,69	1705,81	0,26	111,07	3,09	5,08	34,66	1419,56	0,52	1,14	72,82	28,51	0,40
25/06/2005	274,96	174,41	1095,27	37,19	275,99	1158,91	0,24	93,57	2,50	6,25	26,35	1168,20	0,44	1,52	33,88	40,86	0,29
27/06/2005	21,87	10,85	57,34	6,56	32,76	32,95	0,01	4,43	0,15	0,31	1,46	80,90	0,13	-	3,44	0,42	0,01
02/07/2005	93,27	40,70	169,90	10,13	55,68	243,56	0,04	13,71	0,38	0,87	4,31	231,28	0,08	-	8,51	5,39	0,04
28/07/2005	535,75	401,85	2245,72	70,34	551,98	2256,45	-	187,23	4,71	8,96	54,21	2266,29	1,01	-	61,08	77,48	0,59
29/07/2005	426,91	251,93	1309,68	36,62	416,30	1493,29	0,27	98,01	2,92	7,55	30,05	1303,83	0,63	1,77	35,53	44,54	0,33
10/08/2005	305,44	210,73	1103,40	40,21	302,81	1245,23	-	99,10	2,52	5,02	31,47	1247,44	0,55	1,58	38,79	56,11	0,30
12/08/2005	180,90	103,89	668,66	12,40	162,16	833,61	0,16	37,33	0,89	1,29	10,87	455,18	0,12	0,00	12,03	12,37	0,11
16/08/2005	78,87	27,36	140,38	7,14	52,53	69,59	0,03	9,43	0,26	0,37	2,84	145,12	-	-	5,62	-	0,03
05/09/2005	11,42	3,74	42,29	1,40	6,13	32,95	0,01	2,00	0,08	0,20	0,99	39,78	3,25	0,07	1,07	0,55	0,01

Table 4-g (continued): Chemical data for major and traces elements. PM10 at Las Condes station. Date: 04/10/2004 - 05/09/2005.

Table (4-g): Las Condes (PM 10) ng/m^3

date	**Ge**	**As**	**Rb**	**Sr**	**Y**	**Zr**	**Mo**	**Ag**	**Cd**	**Sn**	**Sb**	**Cs**	**Ba**	**Pb**	**Bi**	**U**
13/01/2004	0,01	0,41	0,47	4,72	0,13	0,60	0,45	0,03	0,02	0,47	-	0,04	6,96	1,37	0,03	0,01
25/01/2004	0,01	0,17	0,31	1,27	0,09	0,42	0,58	0,02	0,01	0,13	-	0,03	4,15	0,79	0,004	0,003
03/02/2004	0,01	0,21	0,33	1,66	0,13	1,16	0,66	0,02	0,01	0,15	-	0,02	5,07	1,05	0,01	0,01
27/02/2004	0,01	0,19	0,39	1,88	0,12	0,89	1,83	0,03	0,02	0,15	-	0,03	6,15	1,34	0,01	0,01
23/03/2004	0,01	0,36	0,25	1,18	0,08	0,50	0,57	0,01	0,01	0,13	-	0,02	4,55	0,83	0,01	0,003
31/03/2004	-	0,02	0,03	0,17	0,01	0,08	0,27	0,01	0,002	0,005	-	0,002	1,36	0,24	0,001	-
22/04/2004	0,0001	0,02	0,03	0,19	0,01	0,08	0,04	0,26	0,003	0,05	-	0,003	1,87	0,27	0,002	-
29/04/2004	0,003	0,32	0,11	0,60	0,03	0,27	1,26	0,24	0,01	0,13	-	0,01	4,12	0,86	0,01	-
30/04/2004	0,004	0,41	0,16	0,95	0,05	0,39	1,40	0,30	0,01	0,21	-	0,01	5,87	1,13	0,01	0,0005
10/05/2004	0,004	0,34	0,21	1,04	0,05	0,44	0,57	0,02	0,02	0,31	-	0,02	6,89	1,64	0,02	0,001
17/05/2004	0,01	0,28	0,30	1,62	0,10	0,66	0,48	0,14	0,01	0,27	-	0,03	9,53	1,26	0,02	0,004
19/05/2004	0,01	0,29	0,19	0,99	0,05	0,49	1,31	0,02	0,02	0,25	-	0,01	5,91	1,46	0,02	0,002
22/05/2004	0,0003	0,02	0,03	0,17	0,01	0,07	0,14	0,32	0,002	0,03	-	0,002	1,94	0,31	0,001	-
20/06/2004	0,01	0,28	0,24	1,36	0,06	0,83	0,67	0,02	0,02	0,41	0,75	0,02	11,06	1,76	0,03	0,004
12/07/2004	0,04	2,67	0,81	5,62	0,25	3,41	4,61	0,12	0,15	2,70	3,73	0,06	46,04	11,09	0,10	0,03
16/07/2004	0,04	2,14	1,27	7,96	0,45	4,70	2,77	0,06	0,07	3,20	5,67	0,13	67,57	10,54	0,12	0,03
21/07/2004	0,01	0,27	0,20	1,36	0,07	0,76	1,28	0,02	0,02	0,28	0,63	0,02	11,41	2,01	0,02	0,00
03/08/2004	0,01	0,62	0,60	37,11	0,05	0,56	0,85	0,05	0,05	0,85	3,35	0,02	14,72	2,01	0,09	0,04
25/08/2004	0,01	0,68	0,46	2,54	0,13	1,14	1,48	0,04	0,02	0,42	-	0,04	12,36	2,79	0,02	0,01
27/08/2004	0,004	0,23	0,10	0,67	0,04	0,30	0,49	0,01	0,01	0,13	-	0,01	3,60	0,85	0,01	-
02/09/2004	0,01	0,69	0,35	1,91	0,10	0,82	1,57	0,09	0,03	0,20	82,34	0,04	10,47	2,01	0,02	0,01
07/09/2004	0,002	0,07	0,05	0,32	0,02	0,18	0,85	0,07	0,01	0,14	98,86	0,004	2,55	0,58	0,01	0,02
14/09/2004	0,01	0,56	0,24	1,15	0,04	0,48	1,38	0,07	0,02	0,17	76,84	0,02	5,54	1,51	0,02	0,01
02/10/2004	0,01	0,40	0,24	1,19	0,06	0,50	0,43	0,06	0,01	0,07	73,10	0,02	5,25	1,09	0,01	0,01

Table 4-g (continued): Chemical data for major and traces elements. PM10 at Las Condes station. Date: 13/01/2004 - 02/10/2004.

Table (4-g): Las Condes (PM 10) ng/m^3

date	**Ge**	**As**	**Rb**	**Sr**	**Y**	**Zr**	**Mo**	**Ag**	**Cd**	**Sn**	**Sb**	**Cs**	**Ba**	**Pb**	**Bi**	**U**
04/10/2004	0,01	0,48	0,37	2,40	0,08	0,64	0,98	0,08	0,01	0,09	58,81	0,04	6,41	1,39	0,02	0,01
12/10/2004	0,002	0,09	0,09	1,16	0,02	0,25	0,30	0,09	0,01	0,10	76,15	0,01	3,28	0,59	0,01	0,003
07/01/2005	0,01	0,21	0,49	2,38	0,15	0,70	1,47	0,03	0,02	0,21	-	0,04	7,50	1,34	0,01	0,01
03/02/2005	0,01	0,30	0,62	3,19	0,17	0,84	1,44	0,04	0,02	0,21	-	0,05	9,58	1,66	0,02	0,01
06/02/2005	0,01	0,19	0,34	1,54	0,09	0,43	0,62	0,03	0,01	0,04	-	0,02	4,19	0,74	0,01	0,004
09/03/2005	0,004	0,18	0,16	0,95	0,03	0,58	1,45	0,00	0,01	0,36	0,13	0,01	6,30	1,21	0,02	0,002
09/03/2005	0,001	0,12	0,04	0,18	0,01	0,16	0,12	0,05	0,004	0,10	68,76	0,002	1,98	0,35	0,01	0,002
30/03/2005	0,02	0,50	0,92	4,71	0,26	1,80	6,91	0,07	0,04	0,78	0,19	0,08	22,03	4,04	0,03	0,02
02/04/2005	0,002	0,11	0,10	0,46	0,03	0,22	0,25	0,21	0,01	0,10	-	0,01	2,56	0,52	0,01	-
23/04/2005	0,005	0,20	0,21	0,99	0,06	0,38	0,55	0,23	0,01	0,17	-	0,02	4,33	0,74	0,01	0,001
27/04/2005	0,05	1,53	1,49	8,50	0,44	3,35	14,69	2,71	0,12	2,33	1,54	0,13	48,20	10,51	0,10	0,03
23/05/2005	0,01	0,43	0,18	0,88	0,05	0,48	0,74	0,0005	0,03	0,72	0,003	0,02	6,80	1,49	0,02	0,001
31/05/2005	0,06	2,54	1,53	9,74	0,50	5,47	6,76	3,00	0,11	4,46	29,81	0,15	74,06	14,50	0,28	0,03
07/06/2005	0,06	1,75	1,27	8,61	0,37	3,55	5,48	1,84	0,08	2,74	2,22	0,12	46,00	8,35	0,09	0,03
25/06/2005	0,03	2,03	0,88	6,13	0,33	4,21	8,40	0,05	0,12	2,11	3,09	0,08	43,34	12,95	0,10	0,03
27/06/2005	0,004	0,20	0,06	0,26	0,01	0,40	0,27	0,01	0,01	0,33	-	0,005	4,53	1,30	0,01	0,01
02/07/2005	0,005	0,57	0,15	0,94	0,05	0,97	1,19	0,01	0,02	0,71	0,81	0,01	11,86	1,78	0,04	0,004
28/07/2005	0,08	2,69	1,86	13,33	0,66	6,38	9,94	0,12	0,21	4,64	6,10	0,21	85,17	22,90	0,15	0,07
29/07/2005	0,04	1,83	1,22	7,50	0,36	4,11	10,35	0,09	0,13	1,96	2,30	0,10	49,69	12,64	0,09	0,04
10/08/2005	0,04	1,97	0,93	6,65	0,50	6,28	11,24	0,07	0,14	2,86	3,68	0,11	46,11	12,91	0,14	0,04
12/08/2005	0,01	0,40	0,42	2,72	0,22	1,68	1,47	0,03	0,03	0,73	0,25	0,04	16,15	2,81	0,03	0,01
16/08/2005	0,01	0,22	0,12	0,57	0,09	1,51	0,62	0,07	0,01	0,27	-	0,01	7,29	0,83	0,02	0,001
05/09/2005	0,001	0,03	0,03	0,21	0,01	0,11	0,23	0,01	0,003	0,02	10,54	0,003	1,64	0,27	0,003	0,001

Table 4-g (continued): Chemical data for major and traces elements. PM10 at Las Condes station.Date: 04/10/2004 - 05/09/2005.

Table (4-h): Las Condes REEs (PM 10) ng/m^3

date	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Hf**	**W**
13/01/2004	0,13	0,26	0,03	0,12	0,03	0,01	0,03	0,004	0,02	0,005	0,01	0,01	0,01	0,02
25/01/2004	0,08	0,18	0,02	0,08	0,02	0,005	0,02	0,003	0,02	0,003	0,01	0,01	0,01	0,06
03/02/2004	0,08	0,18	0,02	0,08	0,02	0,005	0,02	0,003	0,02	0,003	0,01	0,01	0,02	0,002
27/02/2004	0,12	0,26	0,03	0,11	0,02	0,01	0,02	0,003	0,02	0,004	0,01	0,01	0,02	0,01
23/03/2004	0,06	0,14	0,02	0,06	0,01	0,004	0,02	0,002	0,01	0,003	0,01	0,01	0,01	0,04
31/03/2004	0,01	0,02	0,003	0,01	0,002	0,0004	0,002	0,0003	0,002	0,0002	0,001	0,001	-	-
22/04/2004	0,01	0,03	0,003	0,01	0,002	0,001	0,002	0,0003	0,002	0,0002	0,001	0,001	-	-
29/04/2004	0,03	0,07	0,01	0,03	0,01	0,002	0,01	0,001	0,01	0,001	0,003	0,003	0,002	0,0004
30/04/2004	0,04	0,10	0,01	0,04	0,01	0,003	0,01	0,001	0,01	0,002	0,005	0,004	0,01	0,01
10/05/2004	0,05	0,13	0,01	0,05	0,01	0,003	0,01	0,002	0,01	0,002	0,01	0,005	0,01	0,02
17/05/2004	0,08	0,20	0,02	0,08	0,02	0,01	0,02	0,003	0,02	0,003	0,01	0,01	0,01	0,01
19/05/2004	0,04	0,11	0,01	0,04	0,01	0,003	0,01	0,001	0,01	0,002	0,005	0,004	0,01	0,02
22/05/2004	0,01	0,03	0,002	0,005	0,002	0,001	0,001	0,0002	0,001	0,0002	0,001	0,001	-	-
20/06/2004	0,06	0,21	0,02	0,13	0,01	0,01	0,02	0,002	0,01	0,002	0,01	0,01	0,02	0,001
12/07/2004	0,31	0,66	0,1	0,23	0,04	0,02	0,06	0,01	0,04	0,008	0,02	0,02	0,08	0,12
16/07/2004	0,41	1,08	0,11	0,43	0,09	0,03	0,10	0,01	0,1	0,016	0,05	0,04	0,11	0,14
21/07/2004	0,08	0,20	0,02	0,08	0,02	0,01	0,02	0,002	0,01	0,003	0,01	0,01	0,02	0,02
03/08/2004	0,06	0,14	0,01	0,05	0,01	0,004	0,01	0,001	0,01	0,001	0,005	0,004	0,01	0,06
25/08/2004	0,14	0,29	0,03	0,12	0,03	0,01	0,03	0,004	0,02	0,005	0,01	0,01	0,02	0,10
27/08/2004	0,03	0,08	0,01	0,03	0,01	0,002	0,01	0,001	0,01	0,001	0,004	0,003	0,003	-
02/09/2004	0,09	0,22	0,02	0,09	0,02	0,01	0,02	0,003	0,02	0,004	0,01	0,01	0,02	0,04
07/09/2004	0,02	0,05	0,005	0,02	0,004	0,001	0,004	0,0004	0,003	0,001	0,002	0,002	0,01	0,04
14/09/2004	0,05	0,13	0,01	0,04	0,01	0,003	0,01	0,001	0,01	0,001	0,004	0,004	0,01	0,04
02/10/2004	0,06	0,15	0,02	0,06	0,01	0,004	0,01	0,002	0,01	0,002	0,01	0,01	0,01	0,002

Table 4-h: Chemical data for REEs elements. PM10 at Las Condes station. Date: 13/01/2004 - 02/10/2004.

Table (4-h): Las Condes REEs (PM 10) ng/m^3														
date	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Hf**	**W**
04/10/2004	0,08	0,21	0,02	0,08	0,02	0,005	0,02	0,003	0,02	0,003	0,01	0,01	0,01	0,01
12/10/2004	0,03	0,07	0,01	0,02	0,005	0,002	0,01	0,001	0,005	0,001	0,002	0,003	0,01	0,03
07/01/2005	0,14	0,28	0,03	0,13	0,03	0,01	0,03	0,004	0,02	0,004	0,01	0,01	0,01	0,06
03/02/2005	0,19	0,38	0,04	0,17	0,04	0,01	0,04	0,01	0,03	0,01	0,02	0,02	0,02	0,01
06/02/2005	0,10	0,20	0,02	0,09	0,02	0,005	0,02	0,003	0,02	0,003	0,01	0,01	0,01	-
09/03/2005	0,04	0,11	0,01	0,04	0,01	0,002	0,01	0,001	0,01	0,001	0,003	0,004	0,01	0,12
09/03/2005	0,02	0,07	0,003	0,01	0,002	0,001	0,002	0,0003	0,002	0,0003	0,001	0,001	0,003	0,01
30/03/2005	0,27	0,57	0,07	0,29	0,06	0,02	0,06	0,01	0,05	0,01	0,03	0,02	0,04	0,06
02/04/2005	0,03	0,06	0,01	0,04	0,01	0,002	0,01	0,001	0,01	0,001	0,003	0,003	0,001	-
23/04/2005	0,06	0,12	0,01	0,06	0,01	0,003	0,01	0,002	0,01	0,002	0,01	0,01	0,01	0,00005
27/04/2005	0,50	1,04	0,11	0,65	0,09	0,03	0,10	0,01	0,07	0,01	0,04	0,04	0,07	0,13
23/05/2005	0,05	0,11	0,01	0,04	0,01	0,004	0,01	0,002	0,01	0,001	0,005	0,005	0,0003	0,11
31/05/2005	0,51	1,19	0,12	0,47	0,10	0,03	0,12	0,01	0,08	0,02	0,05	0,04	0,12	1,51
07/06/2005	0,45	0,96	0,10	0,81	0,09	0,02	0,10	0,01	0,07	0,01	0,04	0,04	0,08	0,20
25/06/2005	0,42	0,83	0,08	0,39	0,07	0,02	0,09	0,01	0,06	0,01	0,04	0,03	0,10	0,10
27/06/2005	0,02	0,07	0,004	0,04	0,004	0,001	0,00	0,001	0,003	0,0004	0,002	0,001	0,01	0,02
02/07/2005	0,06	0,14	0,01	0,05	0,01	0,004	0,01	0,001	0,01	0,002	0,01	0,005	0,02	0,12
28/07/2005	0,75	1,66	0,18	0,71	0,15	0,05	0,16	0,13	0,03	0,08	0,004	0,07	0,21	0,52
29/07/2005	0,48	0,96	0,10	0,38	0,08	0,03	0,09	0,01	0,07	0,01	0,04	0,04	0,09	0,26
10/08/2005	0,45	0,97	0,10	0,44	0,09	0,02	0,09	0,07	0,01	0,04	0,002	0,04	0,17	0,46
12/08/2005	0,17	0,31	0,04	0,15	0,03	0,01	0,04	0,01	0,03	0,01	0,02	0,02	0,03	0,06
16/08/2005	0,04	0,11	0,01	0,04	0,01	0,002	0,01	0,001	0,01	0,001	0,004	0,003	0,02	0,003
05/09/2005	0,01	0,03	0,002	0,01	0,002	0,001	0,002	0,0003	0,002	0,0003	0,001	0,001	0,002	0,0002

Table 4-h (continued): Chemical data for REEs elements. PM10 at Las Condes station. Date: 04/10/2004 - 05/09/2005.

CHAPITRE 5: DISCUSSION ET CONCLUSION

5.1 Santiago atmospheric pollutions levels

During the last decades, Santiago presents a diminution in PM concentrations in the atmosphere. In fact, there is an annual average PM10 concentration of 77 µg/m^3 (2004/2005) that also exceeds both national and EU standards. Fine fractions present the same decreasing tendencies with time, in Santiago (see chapter 1) as well as in Sao Paulo which has 30 µg/m^3 PM2.5 in wintertime and 15 µg/m^3 in summer time (Castanho et al, 2001), both cities being over EU standard (25 µg/m^3).

Worldwide there is also a tendency in most great cities to have a reduction of pollutant concentrations (Baldasano et al, 2003). For example, in the nineties, PM10 concentrations in Paris, London and New York show a clear decrease below EU standard (40 µg/m^3). This has to be kept in mind when comparing data obtained at various dates. The highest concentration (over 300 µg/m^3) in TSP (total suspended particles) was observed in many cities from Asia and in two from Latin American: Tegucigalpa (652 µg/m^3) and Montevideo (335 µg/m^3) (Baldasano et al., 2003).

In Europe, the PM10 lowest concentrations were observed in Newcastle (17 µg/m^3), in some French cities such as Rennes (16 µg/m^3), Toulouse and Marseille (18 µg/m^3) while the most polluted cities were Rome (52 µg/m^3) and Sevilla (49 µg/m^3) (Baldasano et al., 2003). In Latin America, the PM10 annual average concentration in Mexico City (52 µg/m^3), and the winter (77 µg/m^3) and summer (32 µg/m^3) average concentrations in Sao Paulo all decrease, but remain still over both the EU standard values (Baldasano et al., 2003) and the national standard (50µg/m^3) during the last 20 years (Castanho et al, 2001).

In fact, during the last 10 years (1996-2004/2005) some elemental concentrations observed in PM10 at La Paz station (fig 13, chapter 4), present a diminution: Fe (~3500ng/m^3 to ~1500ng/m^3), Ca and Al (~3000ng/m^3 to ~1200ng/m^3), K (~1000ng/m^3 to ~500ng/m^3) and Mg (500ng/m^3 to 200ng/m^3). This tendency is also observed at the Las Condes station (fig 12, chapter 4). On the other hand, in the town center, some trace elements also present an important diminution, for example Pb and Zn (250ng/m^3 to < 50 ng/m^3), As (70 ng/m^3 to 5 ng/m^3) and some constant concentrations in Cu and Mn (~100 ng/m^3) (fig 13, chapter 4). Therefore, this tendency is probably an answer to different policies, implemented in order to decrease the level of pollutions (see 5.4).

Nevertheless, the PM2.5 features in Santiago through time show a constant concentration in major elements (Al, Fe, Ca, K and Mg) with the exception of Al in La Paz (800ng/m^3 to 250 ng/m^3) (fig 12 and 13, chapter 4) . However, some trace elements such as the arsenic diminish from 50ng/m^3 to 15ng/m^3 and the concentrations in Pb at La Paz (180ng/m^3 to 40 ng/m^3) are two times higher than those observed at Las Condes (80ng/m^3 to 20ng/m^3). With this being said, both stations present constant values for Zn (120ng/m^3), Cu (40ng/m^3) and Mn (20ng/m^3), between 1996 and 2004/2005. This tendency observed in PM 2.5 could indicate anthropogenic sources.

5.2 Sources Identification

The objective of the present thesis is to supply and examine new data about the characteristics of atmospheric aerosols over Santiago de Chile, to interpret them in terms of origin, processes and potential impact on human health. In this study, combined SEM and ICP-MS data processed using improved geochemical and statistical methods, supply supplementary information with respect to former results.

In this thesis, we have performed mineralogical and morphological analyses of aerosols (202 samples collected in 2004 and 2005), geochemical analysis (104 samples collected in La Paz station and 98 in Las Condes) from 2 collection sites. These analyses are complementary to the previous ones already published by Artaxo and have contributed additional aerosol samples collected in 2004 at other monitoring stations.

Both mineralogical and morphological data (Morata en al., 2008) and the FA-PCA processing of our chemical data, demonstrate that most particles have a lithogenic origin, as they display EDS spectra compatible with typical spectra of volcanic rocks and soils minerals. Lithogenic particles occur mainly in the PM10 fractions, and are typically found in residential sites. On the contrary, anthropogenic particles mainly occur in the PM2.5 fraction, and are typical of central areas of Santiago. Anthropogenic particles display specific shapes (mainly spheres and slates) and have to be related to both the high enrichment factors (> 10^x) X= 10^3-$10^{6,}$ of metals such as Cu, Mo, Pb and Sb and multi-metals associations identified from FA-PCA processing and interpreted as representative of different pollution sources.

Most of the sources identified in the present research are consistent with those identified in previous studies on Santiago and in cities from the central valley (table 6 and 7, chapter 4). We have identified sources with regional impact (lithogenic or marine, copper industries) and local sources. We have discussed the specific impact of these sources on the two sites we studied Finally, we have evaluated to potential for rare earth elements to be tracer of new contaminations in urban environments and have evidences that these REEs powerful tools that permit to identify sources that were not identified before, such as traffic (through catalytic exhaust pipes) and FCC (fluid catalytic crackers) combustion.

5.2.1 Natural sources of elements

We found in a first study (Morata et al., 2008; chapter 3) that Si, P, Ti, Ca are issued from the surrounding geological formations, soils and dusts. In a second one, (chapter 4), we identified typical geochemical associations including Ca and Ti, together with Fe, Mg, Y, Zr, U, Sr, and V. These elements are likely to be controlled by two natural sources, the main one being lithogenic and marine source being the minor one.

Morata et al, (2008) suggested for chlorine an anthropogenic origin related to industry, ruling out the hypothesis of an oceanic origin. In contrast, our statistical analysis associates Mg, Na and Cl and suggests a marine aerosols origin. This later hypothesis is supported by Kavouras (2001), Hedberg (2005) and Moreno (2010). However, due to the lack of data, it was not possible to suggest a secondary involvement of metallurgic processes in the Cl source.

5.2.2 Anthropogenic sources of elements

According to enrichment factors, the first association of elements with a clear anthropogenic origin (S, Cl, Cr, Cu and Zn) has been confirmed and completed by another list of elements including Rb, K, Cs, Fe, P, Ba, Mn, Ni, Co, Sn, Pb, Mo, Cd, As, Ag, and Sb. These elements are controlled by different pollution sources identified mainly by FA-PCA analysis.

5.2.2.1 Copper industry

We suggest that **copper production** (mine, smelter process and refinery), traced by Cu and associated released metals Zn, Mo, As and Pb, is a source with regional impact. It is related to several mines and production centers located about 100 km around Santiago. This source has been already identified by Artaxo et al., 1999 in Santiago, but it is the first time that the elements Zn, Pb, Bi, Ag, Ba, Cd, Fe, Mn were detected and associated to copper smelter in Santiago. This is due to the high sensibility of the analytical procedures we applied. SEM observations of Cu-S grains may confirm the occurrence in the breathable air of Santiago of copper industry-related particles. However, one cannot rule out the hypothesis of secondary sulfates as a source for these Cu-S grains. Morata et al, (2008) suggested these Cu-S particles to be sulfates due to the lack of correlation between Cu, Zn and S. New SEM observations on 2004/2005 samples (chapter 3) show the presence of S and Cl in the majority of the analyzed samples. We interpreted the association of S with Cu, Zn or Fe as sulfide phases emitted by *copper smelters*. It can be noted that Zn has been related by Artaxo et al. (1999) and Moreno et al. (2010) to oil combustion or industry emission while we propose copper smelter as emission source for Zn in Santiago.

5.2.2.2 Coal /Oil combustion

We recognized at Las Condes a coal combustion source associated with Sb, Pb, As, Zn, Cr and Co in accord with Moreno et al. (2007).V and Ni are widely accepted as trace elements of oil combustion. We demonstrate that REE can be used for tracing certain types of oil combustion.

5.2.2.3 Burning biomass

Our results confirm K and Rb to be tracers of biomass burning (Kavouras et al., 2001). The association between Zn and K is related to wood burning (Hedberg et al., 2005) and is detected in the residential Las Condes area.

5.2.2.4 Iron oxides and steel industry

This source has not been identified through any statistical study, neither ours or other authors ones. Thus Fe is interpreted as either lithogenic or linked to copper industry. But different Fe oxides have been characterized by SEM observations (Morata et al, 2008 and new observation (see 3.4, chapter 3)) in both stations and fractions (table 10).

Anhedral particles are either magnetites or goetites as determined by their magnetic properties (Silva, 2005) and could have a lithogenic origin. But, Fe oxides could come from iron weathering (Fe bars, tiles, grating equipment, exhaust pipes) as noted by Morata et al, 2008. These origins are also consistent with factor analysis results where Fe appears related to *crustal origin*, but also to *copper smelter* (table 5) as stated in Valdes et al, in preparation.

Sphere of Fe oxides 0.5-1µm have been observed (Morata et al., 2008 and more recent observations, see 3.4 chapter 3), probably produced through high temperature industrial processes (Sandoval et al, 1993). Steel industry is present all over Santiago, representing 55% of the total smelting plants. Thus we propose, mainly based on SEM observations, that steel industry is responsible of the high temperature Fe oxide micro spheres.

5.2.2.5 Calcium carbonates and sulfates

Both were described by Morata et al, (2008), who proposed either a lithogenic (sedimentary) or an anthropologic origin for these minerals, as both quarries and plaster industries exist around Santiago. A lithogenic origin is in agreement with our FA treatment which associates Ca with crustal source. On the other hand, the relation between Ca and S suggest a secondary formation of sulfate as proposed by several authors (Kavouras et al., 2001; Moreno et al., 2010). The possible oxidation of SO_2 emitted by anthropogenic sources (Moreno et al., 2010, Kavouras et al., 2001) and its reaction with Ca^{+2}, Ba^{+} was proposed by Morata et al, (2008).

Some of the sources identified in the present study (crustal, marine, oil combustion, traffic) were also identified by Castanho et al, (2001) in Sao Paulo. The percentages of contribution of each source in both cities are similar, with 30 % re suspended dust contribution in Sao Paulo and 25% in Santiago while traffic contributes for 26% and 16%. Oil combustion contributes with 20% in Sao Paulo and 14% to 20% (colder months) in Santiago. The sulfate source has a similar contribution (~ 20%) in both cities and the industry contribute to 4% in Sao Paulo while in it Santiago represent ~30% of PM10 and PM2.5 (see fig 10, chapter 1).

Source **Author and year of sampling**	**Natural Sources**		**Combustion**		**Transport/ automobil emissions**	**Sulfate/ secondary sulfate**	**Copper emissions**	**Biomass/ Wood burning**	**Industry emissions**
	Dust	**Sea**	**Oil**	**Coal**					
Valdes [1] **2004, 2005**	**$PM_{2,5}$**: **Al**, **Ca**, Fe, **K, Rb, Sr, V, Ti, Zr**. Ba, Cr, Mo, Zn.	**$PM_{2,5}$:** **Mg, Na.**	**$PM_{2,5}$:** **V**, **Ni**.	**$PM_{10-2,5}$ - $PM_{2,5}$:** Sb, Pb, As, Zn and Co; Cr	**$PM_{2,5}$:** Mn; REE.	**Based on SEM observations:** Particles Ca-S, Ca-S, Fe-S, Cu-S, Pb-S, Zn-S.	**$PM_{2,5}$:** **Cu**, Zn, **As, Mo, Pb, Bi, Ag, Ba, Cd, Fe, K, Mn.** Al, Cr, Rb, Sr, V,Ti, Zr.	**$PM_{2,5}$:** **K.**	***steel Industry: (based on SEM observations)** sphere of Fe particles ~2µm.
Artaxo (1996)[2]	**$PM_{2,5}$**: **Al, Ca, Fe, Si, Ti, Sr, Mn** (Pb, As, P).		**$PM_{2,5}$** : **V, Ni, S, Zn, Cl, Mn**.		**$PM_{2,5}$:** **Br,Pb,Cl,** K and Sn.	**$PM_{2,5}$:** **S, Se, K, P.**	**$PM_{2,5}$**: **S**, **Cu, As, Mo, K, P.**	**$PM_{2,5}$:** Zn, Cu.	**$PM_{2,5}$:** Zn, Cu.
Moreno[3] (1998-2007)	**$PM_{10-2,5}$-$PM_{2,5}$**: **Al, Ca, Si, Ti**. **$PM_{10-2,5}$:** **Fe**, **Mn**, **Mg, Sr.**	**$PM_{2,5}$:** Na, Cl. **$PM_{10-2,5}$**: Na, Cl, (Mg).	**$PM_{10-2,5}$- $PM_{2,5}$**: **Mn, Cu, Fe, Zn,** Pb. **$PM_{10-2,5}$**: **Ba, Cr**.		**$PM_{2,5}$**: **Br**, **Pb,Cl**, K, (~S).	**$PM_{2,5}$:** **S, P.**	~S		
Morata[4] (2004)	**$PM_{10-PM2,5}$:** **PIXE: Al, Ca, Fe, Si.**				**SEM**: FeO.	**PIXE**: S S-K/Ca S- (Fe,Mn, Cr,Ti). **SEM:** $CaCO_3$, $CaSO_4$, $BaSO_4$.	S		

Notes: [1]Valdes et al., (in preparation); [2]Artaxo et al., 1999; [3]Moreno et al., 2010 and [4]Morata et al, 2008.

Table 10: Principal sources identified in Santiago through statisticall anlysis and SEM observation. Chemical signatures are compared for Santiago. Both tables regroup sources identified as either regional or local, natural or anthropogenic. In these tables, elements that are common to all authors are underlined; elements in bold have been considered by each author as typical of a given source, while the others represent secondary elements mentioned by the authors.

5.3 Influence of meteorological conditions.

We observed specific meteorological conditions associated with very high pollutant concentrations during the days analyzed. The maximal elemental concentrations correspond to configurations of low pressure and temperature associated to cloudiness days (BPF) and also during the mix system (H-BPF) while the smaller concentrations are related to sunny days, high pressure and temperature.

During this analysis we found the signal of “copper industry” on Santiago, which was stronger in the eastern part of Santiago. Inside of this signal we also noted high concentrations in arsenic with concentrations over 3 times the standard levels fixed. This new observation, which is based on very few days (4 type H episodes, 6 type BPF and 4 of mixed

H-BPF), would need further investigation through a systematic study of the more highly polluted days of each month.

5.4 International norms for elemental concentrations and effectiveness of environmental policies

The WHO and EC have determined the following maximum acceptable concentrations: Pb: 150ng/m^3, Ni: 20ng/m^3, As: 6ng/m^3 and Cd: 5ng/m^3. In contrast, Chilean governmental agencies did not define any norm, except for Pb (0.5 µg/m^3 N). Our results show that average annual concentrations during the years 2004 and 2005 are below the WHO and EC standards. However, as we have previously stated, during winters daily concentrations can overcome maximum accepted levels (As for example, see fig 13 in chapter 4).

The association between total mortality and Cu and Zn has been demonstrated by Cakmak et al, 2009, while Valdes et al., 2011 (in preparation, see in appendix A) describe the relationship between respiratory mortality and Zn and Cl and chronic obstructive pulmonary disease with Ni. It is evident that copper production and oil combustion have impacted Santiago by worsening the quality of life of the habitants. It is thus fundamental to identify without any ambiguity, the source of these toxical elements in order to fight against their emitters.

Since 1996; diverse policies have been implemented in order to improve the air quality in Santiago as it was found to be saturated in pollutants. Two years later the Planning of Prevention and Decontamination to Atmosphere (PPDA) was set up and implemented. The objective was to diminish the concentration of pollution according to WHO standards over the next 15 years. This program was implemented in two stages: from 1998 to 2004 and from 2006 to 2011. The industry and transport sectors are the ones which induced most of the improvements observed during the first stage with respect to the new policies. In fact, the introduction of natural gas (NG) induced a significant decrease in PM and SO_2 emitted by the industrial sector. Since 2004 however, the restriction in NG importations has produced an increase in the use of heavy petroleum and this had negative consequences on air pollution. Nevertheless, reductions of S concentrations in diesel since 2000 have improved air quality. Complementary programs of PM reduction were applied to boilers and heating and SO_2 reduction was compulsory from heavy industry. In the transport sector, even though the number of vehicles increased from 800 000 to more than 1 millon between 2001 and 2005, the air quality standards applied to vehicles, in particular catalytic convertor legislation, mitigated negative impact on air quality. In contrast, the number of public transport vehicles were constant (~8000) during this period. The introduction of unleaded gasoline since 2001 aided the effort to control emissions from this sector (table 11).

Sector	Combustibles and standard levels	1998	1999	2000	2001	2002	2003	2004	2005
Transport	gasoline	leaded gasoline unleaded gasoline							
	Diesel	1000 ppm S		300 ppm S				50 ppm S	
	Standard level to vehicles and taxis, * bus ** truck	EPA 1991 **EPA 1994 **EURO II (1998)				*EPA 1998 *EURO III (2002)		EPA 1994 EURO III Gasoline (2005) Tier 1 california EURO IV Diesel (2005)	
Industry	Natural Gas	Natural gas supply						Natural gas supply restricted	
	Heavy petroleum	Heavy petroleum with higher than 10.000 ppm of S						10.000 ppm S	
	Diesel	1000 ppm S		300 ppm S				50 ppm S	
	MP	Emissions from boilers 56mg/m^3						Emissions from boilers 32 mg/m^3	
	SO_2							Program of reduction of SO_2 applied to heavy industry (>100ton/year)	

Table 11: Policies implemented since 1998 to 2005

5.6 Limitations of the environmental policies

In our study we can see the direct effect of these different policies on PM, major and trace elements concentrations. However, it seems that these reductions only had a limited effect on some trace elements such as a Cu, Mn and Zn, which belong to the “copper smelters” association, whose concentrations are constant with a tendency to increase from 1996 to 2004/2005. In fact, since 2000, Chile leads the international copper market in terms of refined copper production with more than one million of tons/year and 5% annual growth (www.editec.cl). This growth is stimulated by the constantly increasing price of copper (1.67 cents/pound as a maximum). In 2005, CODELCO produced 1.831.183 metric tons of refined copper, equivalent to 30% of the total tonnage produced in 2005 by the major productions (China, India, Russia, Australia, Iran, Poland and USA). This refined copper comes from

Central and North Chile. The principal mines and copper smelters in the Central Region (El Soldado, Andina, Los Bronces, Chagres and Teniente) produce more than 1000 tons: this is equivalent to the total tonnage produced in 2005 by CODELCO in one of the largest Cu open-pit mine in the world: Chuquicamata in Northern Chile. Similarly, the central region produces 10 tons of Mo while 13 tons are produced in North Chile.

Other elements, linked to petroleum combustion (Cr, Ni and V) also appear not to be affected by existing policy. Here it is linked to the combination between the international oil market and the bad diplomatic relations between Argentina (who sells natural gas to Chile) and Chile. During harsh winters, when Argentina does not deliver to Chile the contracted amount of gas, industries and individuals use any fuel they can buy. This induces the emission in the atmosphere of all oil - related chemical elements.

5.7 Limitations of our study and perspectives

From our study, even if some progresses have been made, some polluting sources do not have clearly identified chemical signatures. This is a limitation before future policies could be made effective and set up tighter controls on the emission and measurements of trace elements specific associations.

It is crucial to decipher the origin of some elements whose associations correspond to 2 or more source types. As an example, Zn can be produced either through oil combustion or during copper smelting. S has been observed in the emissions of most pollution sources, but it is difficult to determine its specific origin in each site and case. And obviously it is very important to know which step of the Cu processing (mine, smelter, and refinery) is responsible for Cu pollution in order to fix policies. Therefore isotopic analysis will have to be done in the future, in order to allow the discrimination of trace element sources and their contribution to the chemical signatures found within and around Santiago.

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ANNEXE : IMPACT SUR LA SANTE PUBLIQUE

A.1 Introduction

L’objectif principal de cette thèse a été l’identification des sources polluantes à travers des traçages d’éléments chimiques afin d’identifier leur origine et les processus de génération principaux. Il s’agit d’un pré-requis pour aborder le problème de l’impact de ces polluants en terme de santé publique, et fournir des outils pour faire évoluer les politiques publiques.

Ce présent travail de thèse a permis entre autres, de quantifier les niveaux et variations des concentrations en éléments chimiques potentiellement toxiques. Il a de même contribué à identifier les sources responsables de ces concentrations élevées de polluants à Santiago de Chile.

L’objectif de ce travail annexe est d’établir statistiquement l’impact d’une augmentation de concentration de certains métaux en terme de santé publique, en prennant comme critère le taux de mortalité dû à des pathologies cardiaques ou respiratoires.

Un travail en collaboration avec le département d’Epidémiologie et Environnement de l’Université d’Harvard a été développé dans le cadre de la présente thèse. Ce travail a été effectué à partir d’une base de données robuste du Ministère de la Santé du Chili, qui regroupe des données journalières de concentrations en éléments chimiques (Na, Al, Si, S, Cl, K, ca, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Pb) mesurées dans la fraction PM2.5 du matériel particulaire de Santiago, et des données de mortalité liés aux pathologies cardiaques et pulmonaires, sur une période de 8 années (1998-2005).

Ce travail est présenté sous forme d’un pré publication.

ORIGINAL ARTICLE

A.2 Associations between Cause - Specific Mortality and Elemental Concentrations of Ambient Particles (PM2.5) In Santiago, Chile. To be submitted to….

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Running head Elemental PM and mortality in Chile

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Objective: The health effects of particulate air pollution are widely recognized and there is some evidence that the magnitude of these effects vary by particle component. Therefore we studied the effects of ambient fine particles (aerodynamic diameter <2.5µm, PM2.5) and their components on cause-specific mortality in Santiago, Chile, where particulate pollution is a major public health concern.

Material and Methods: Air pollution data was collected in a residential area in the center of Santiago. Depending on the season measurements were performed daily, or every two or three days in 1998-2005. Daily mortality counts were obtained from the National Statistic Institute. The associations between PM2.5 and cause-specific mortality were studied in time series analyses using Poisson regression in R. The effect of elemental components of particles and mortality was studied using a two stage hierarchical method introduced by Franklin et al.,[1] In the models we controlled for time trend, day of the week, temperature and dew point temperature.

Results: During months when the sulfur content of the PM2.5 mass was high, there was a 2.1% increase (95% CI: 0.9-3.5) in cardiovascular mortality for 10 $\mu g/m^3$ increase in PM2.5, compared to 0.85% increase (95% CI: 0.33-1.38) in association with PM2.5 overall. Particles with high content of zinc or chloride showed stronger associations with all respiratory mortality than did PM2.5 alone. High nickel content of PM2.5 amplified the association between PM2.5 and COPD. Overall, the associations were stronger for respiratory than for cardiovascular outcomes.

Conclusions: Our findings suggest that sulfur, zinc, chloride and nickel may be elements related to greater health effects than PM2.5 mass alone in Santiago, Chile. The sources of particles containing these elements need to be determined to better control the emissions of these harmful particulates.

Key words: air pollution, composition, element, particulate matter, mortality

Introduction

Particulate air pollution is a main environmental risk factor for human health, and short-term associations between mortality and particulate pollutants are well established.[2-4] Some studies have suggested that the magnitude of the association between mortality and particles differs by particle size, with fine particles (particles with aerodynamic diameter less than 2.5µm, PM2.5) having greater effects than larger particles (diameter between 2.5-10µm, coarse particles.[5-7] However, regional and seasonal differences in the health effects of particles have also been reported.[8-10] Composition of particles also varies by season, suggesting this may play a role in the toxicity of particles. Due to the lack of data on particulate composition, the health effects of specified particulate components have not been widely studied, and most epidemiological studies performed on a population level have been from the United States.[1,11-13] Studies that control for seasonal temperature as a surrogate for ventilation rate have identified sulfur, nickel, and vanadium as particularly toxic,[1,11,12] while studies that ignored confounding by seasonal temperature have reported more mixed results.[14,15] By identifying the elements most toxic to human health, we can move to more efficient regulations for particulate matter. Therefore confirming these associations, particularly in other parts of the world, is important.

In Santiago, Chile, air pollution is a major public health concern because of its dense population and the geography of the area.[16] The city is located between The Andes Mountains at the East and Coast Mountains at the West. In the center of Chile, during the majority of the year there is a thermal inversion layer and during autumn and winter there is an inversion layer produced as a result of cooling of the ground. When these phenomena coexist, the conditions became very favorable to accumulation of pollution, and the levels of particulate matter often exceed the regulations set by U.S. Environmental Protection Agency and World Health Organization (WHO).[17,18] Previous studies provide evidence that particulate pollution in Santiago increases the risk of mortality [5,19,20] and morbidity. [21,22] The most recent studies were also able to differentiate the health effects of more specified components of particles.[19,23] Unfortunately, as in the U.S. PM2.5 mass components in Chile were not measured on a daily basis, hence the data are sparse, and time series analyses have weak power. Cakmak et al.,[19] applied a time series analysis to the PM2.5 components, but they only had 655 observations over the years 1998-2006. Most of the previously published papers have used source apportionment methods to examine the effects of source-specified PM2.5. In these studies, authors have found that particles from mobile source, including elemental and organic carbon components, have the strongest association with total, cardiac, and respiratory mortality and morbidity in Chile.[19,23]

We have previously introduced a methodology to take better advantage of the complete data, specifically that while speciation data only exist every 3-6 days, PM2.5 is monitored more frequently, and mostly daily. The method was applied to U.S. mortality and morbidity data by Franklin et al., [1] and Zanobetti et al.,[12] where in the first stage we fit a daily time series analysis using every day, and the PM2.5 data, and in the second stage we look at how the relative fraction of PM2.5 from different elements in different time periods modifies the PM2.5 association. This same approach was subsequently adopted by Bell et al.,[11] In this study we have chosen to let the PM2.5 coefficients vary by month, and used the monthly ratios of components to total mass to explain the variations in those coefficients.

We applied this approach to cause-specific mortality during years 1998-2005. Different elements (Aluminium (Al), Sodium (Na), Silicon (Si), Sulfur (S), Chloride (Cl), Calcium (Ca), Chromium (Cr), Manganese (Mn), Nickel (Ni), Potassium (K), Iron (Fe), Copper (Cu), Zinc (Zn), Selenium (Se), Bromine (Br), Lead (Pb), of fine particles were extracted, and the associations with mortality for all cardiovascular (CVD), all respiratory, cerebrovascular, and chronic obstructive pulmonary disease (COPD) were studied separately.

Material and Methods

Air Pollution and Meteorological Data

The PM2.5 mass and species concentration data were obtained from Parque O'Higgins, one of the 7 air quality monitoring stations of the Automatic Monitory of Atmospheric Contaminants Network (MACAM NET). This station is located in the center of Santiago in a residential area in one of the main green areas in Santiago. East of the station is the Principal National Route "Carretera Panamericana" and to the west is the University of Chile Campus. In each of the network stations the level of particulate matter is measured systematically. In three of these stations temperature, humidity, solar irradiation and wind direction are also measured. The information is stored in a data base called: AIRVIRO, maintained by the National Centre of the Environmental Department.[24]

Particulate matter was collected on 37mm diameter Teflon filters (Pall Flex) [24] by a gravimetric method using a Dichotomous sampler (Sierra Andersen 244, Smyrna, GA). This method allows the collection of particle sizes smaller than 2.5 µm (fine fraction), and in the range 2.5–10 µm (coarse fraction) with a bulk flow rate of 16 – 18 l mn^{-1}. This semiautomatic equipment is programmable for sampling periods of 24 hours, and it allows the simultaneous collection of the two particulate fractions. The samples were collected from 10:00 a.m. to 10:00 a.m. the next day in autumn and winter, and from midnight to midnight in spring and summer. The measurements were performed daily from April to September, every two days in October, November and March, and every three days in December, January and February from 1998 to 2005.

The physical conditioning of the filters was performed in the gravimetric laboratory at the department of public health of the ministry of health of Santiago, Chile (Subsecretaría de Salud Pública del Ministerio de Salud de Santiago de Chile). Filters were weighted before and after use on electronic microbalance, Precisa (Swiss) 40SM-200A, allowing 1 µg error, and stored in individual plastic boxes in dry chambers. The laboratory atmosphere had a 50% controlled relative humidity and temperature between 20°C and 25°C.

The elemental analyses for the PM2.5 filters were conducted using X-ray fluorescence (Desert Research Institute). The analytical methodology for analyzing the elements has been described in Sax et al.,[25]

Based on the results from previous epidemiological studies [19] [26] we focused on the species with different sources and toxicological background. We examined the following species: Aluminium (Al), Sodium (Na), Silicon (Si), Sulfur (S), Chloride (Cl), Calcium (Ca), Chromium (Cr), Manganese (Mn), Nickel (Ni), Potassium (K), Iron (Fe), Copper (Cu), Zinc (Zn), Selenium (Se), Bromine (Br), and Lead (Pb).

Health Data

The number of daily deaths in Santiago, with a population of 6 million inhabitants, was obtained from the National Statistic Institute for years 1998 to 2005. The causes were classified according to the International Classification of Disease, 9th Revision (ICD-9). We examined daily mortality counts of respiratory diseases (ICD-9: 460-519), cardiovascular diseases (CVD, ICD-9: 390 - 429), chronic obstructive pulmonary diseases (COPD, ICD-9: 490-496) and cerebrovascular diseases (cerebro, ICD-9: 430-459).

Statistical Methods

We applied a time series analysis using Poisson regression to examine the association between daily counts of cause-specific mortality and daily PM2.5 mass concentrations. The model controlled for seasonality and long term trend with a penalized spline with 5 degrees of freedom (df) for each year; day of the week using indicator variables; same day temperature with a penalized spline with 3 df and relative humidity.

Because particle species were not measured every day we first fit a time series analysis of daily PM2.5 and daily counts of cause-specific mortality. We also computed the mean monthly ratios of the of species concentrations to the total PM2.5 mass. In the model we included an interaction term between PM2.5 and the mean ratios of individual elements to PM2.5 mass, averaged over each month of each year. This allowed us to see whether the PM coefficient was systematically higher or lower when more (or less) of the PM mass was a particular element.

The effect estimates are expressed as a percent increase in mortality for a 10µg/m^3 increase in the same day PM2.5 mass concentration. From the interaction we computed the % increase in cause-specific mortality per 10 µg/m^3 increase in PM2.5 for an increase in the species to PM2.5 mass proportions from the first to the third quartiles. We used SAS 9.1 [27] for data management, and R 2.7.2 [28] for regression modeling.

Results

In Santiago, Chile, there were 54,924 deaths from all cardiovascular diseases, 21,573 from all respiratory diseases, 6,528 from COPD and 16,968 from cerebrovascular diseases over the years 1998 to 2005. Table 1 shows the distribution of the mortality by cause, together with the distribution of the weather variables and PM2.5 that had a median concentration of 33 µg/m^3. The distribution of the concentration ratios of species to the total PM2.5 mass is presented in Table 2.

The associations between cause-specific mortality and PM2.5 were significant for all of the causes analyzed. The strongest effects were observed for all respiratory mortality with a 1.24% increase (95% CI: 0.45- 2.03), and for COPD mortality with 3.14% increase (95% CI: 1.85 - 4.45) for a 10 µg/m^3 increase in PM2.5 (Table 3).

Figure 1 **s**hows for each cause of death the results for PM2.5 together with the effect of the species on modifying those effects. When we included the interaction term for PM2.5 and the elements, we found that higher sulfur concentrations increased the effect of PM2.5 on cardiovascular mortality. Specifically, we found a 0.92% increase in CVD mortality (95% CI: 0.4? add decimal-1.5) per 10 µg/m^3 increase in PM2.5 in months when the fraction of sulfur in the total PM2.5 mass was at the lower quartile versus a 2.1% increase (95% CI: 0.9 add decimal-3.5) in months when the fraction of sulfur in the total PM2.5 mass was at the higher quartile (Figure 1). Sulfur also modified the association with cerebrovascular deaths, with a 1.0% increase in cerebrovascular mortality (95% CI: 0.1 decimal-1.9) per 10 µg/m^3 increase in PM2.5 at the 25%tile versus a 2.2% increase (95%CI 0.2 decimal- 4.2) at the 75%tile.

Zinc, chloride and nickel modified the association between PM2.5 and death from all respiratory and COPD. Specifically, at the 75%tile of Zn concentrations PM2.5 was associated with a 1.7 % increase (95% CI: 0.8 add decimal -2.7) in all respiratory mortality and at the 75%tile of Cl concentrations with a 1.5% increase (95% CI: 0.6 decimal-2.4) per 10 µg/m^3 increase in PM2.5.

Ni and Zn also modified the association of PM2.5 with COPD mortality. At the upper 75%tile we saw, respectively for Ni and Zn, a 3.3% increase (95% CI: 1.9-4.7) and a 4.4% (95% CI: 2.8 - 6.0) per 10 µg/m^3 increase in PM2.5.

Discussion and conclusion

In Santiago, Chile, we found that PM2.5 was associated with all cause and cause specific mortality. The effect size per 10 µg/m^3 of PM2.5 we saw was almost identical to that reported by Zanobetti and Schwartz in an analysis of over 100 U.S. cities.[29] This confirms those associations are applicable elsewhere.

In examining the composition of fine particles, we found that sulfur, a marker for sulfate particles, was specifically associated with higher than average toxicity for cardiovascular and cerebrovascular deaths, while zinc, chloride, and nickel had higher than average toxicity for respiratory mortality. For all the elements, the point estimates were consistently greater for respiratory than cardiac effects.

The associations we found between PM2.5 and cause-specific mortality were consistent with previous literature of studies done in Chile [20,21,30] and in the US.[29] In regard to the elemental concentrations of fine particles, we found a clear relation for CVD and cerebrovascular mortality with S; while zinc and nickel were associated with higher than average toxicity for respiratory and COPD deaths. Increased cardiovascular mortality has previously been linked to increases in the levels of EC, OC, nitrates, sulfates, potassium, copper and iron in California.[31] In line with our findings, an earlier Canadian study has also reported associations between total mortality and sulfate ion, nickel and zinc [32].

Due to the fact that the PM components have been available only for one day in three or six, some studies in the US have used a method similar to the one presented in this study and showed that PM chemical components modify the PM effect to mortality[1,13] or hospitalization.[11,12] Among these studies, the elements that have most often been found to increase the health risk are Nickel, Vanadium, Aluminum, Arsenic, Sulfate, Bromine, and Silicon.

The effects of particulate species on total mortality in Chile have been studied by Cakmak et al.,[19] They found associations between mortality and organic carbon (OC) (RR 1.07; 95% CI 1.06-1.07), Cu (RR 1.06; 95% CI 1.05-1.08) and Fe (RR 1.05; 95% CI 1.04-1.06, but they only had 655 observations over the nine years of study. Cakmak and co-authors[19] found also that soil-related particles included elements Al, Ca, Fe, and Si, and that these particles had weaker but statistically significant mortality effect.

In an earlier study on the effects of particulate components and sources on emergency department visit counts in Chile, particles related to combustion sources included elements such as Cr, Cu, Fe, Mn and Zn, and they were associated with total and respiratory visits.[23] The association between respiratory morbidity and factor containing Zn is consistent with the current results, however; we found no clear associations between mortality and soil-related particulate elements Al, Ca, Fe or Si.

The identification of the emission sources of these metals is one of the central problems to discuss. In the current study, sulfur was associated with higher cardiovascular mortality than the total PM2.5 mass, and in a previous study, sulfur has been related with the emissions from smelters.[33] In fact, one of the potential sources in Santiago is a large copper smelter Caletones that burdens oxidized sulfur in the Santiago basin and further produces sulfur rich fine particles.[34] The sources for Ni and Cl are widely related with combustion and traffic processes,[35] and Zn has been categorized as combustion related element along with Cr, Cu, Fe and Mn.[23] The harmful particle sources identified by Cakmak et al.,[23] are consistent with the ones previously recognized by Artaxo et al.,[35] They found that the principal source of Zn is oil combustion in particular, while Hedberg et al.,,[33] and Kavouras et al.,[36] related Zn with the copper smelter. In addition, the relationship between Zn and K also has been interpreted has a tracers of wood burning.[33] The contradictory results are possibly related to local differences in particulate sources. This underlines the importance of determining the health effects of particulate matter at various locations by elements.

In Chile there is an ongoing work related with identification of particulate sources; however, there are not many studies that show the relationship between public health problems and specimen elements and their sources of emission. As future prospect, the use of isotopes can help tracing the sources in urban air pollution. This would allow distinguishing between the different sources associated to specific elements such as Zn, S, and Cu.

There are some limitations to this study. One is that the data collection for the particulate matter was not continuous throughout the year, and daily data was available only for the winter months from April to September. The air pollution data was also collected at one measurement location, which may cause some exposure misclassification. However, having data from only one measurement station may lead to Berkson error, which reduces the power to reveal significant effects[37] and therefore leads rather to an underestimation than overestimation of the health effects of particles.

In conclusion, it seems that PM2.5 mass alone is not a sufficient metric when evaluating the health effects of PM exposure. Our findings suggest that sulfur, zinc, chloride and nickel may be elements related to greater health effects than PM2.5 mass in Santiago, Chile. The sources of particles formed of these elements need to be determined in order to better control the emissions of these harmful particulates.

Tables

Table 1. Distribution of daily cause-specific mortality, PM2.5 and weather variables in Santiago, Chile, for the years 1998-2005.

Cause of death	Percentile				
	5th	25th	50th	75th	95th
Cardiovascular	11	15	19	23	29
Cerebrovascular	2	4	6	8	10
All respiratory	2	5	7	10	16
COPD	0	1	2	3	5
Environmental variables					
PM2.5 (µg/m^3)	13	21	33	55	89
Ambient Temperature (C°)	8	12	16	20	23
Relative humidity (%)	38	51	63	76	88

Table 2. Distribution of the species- to-PM2.5 mass proportions

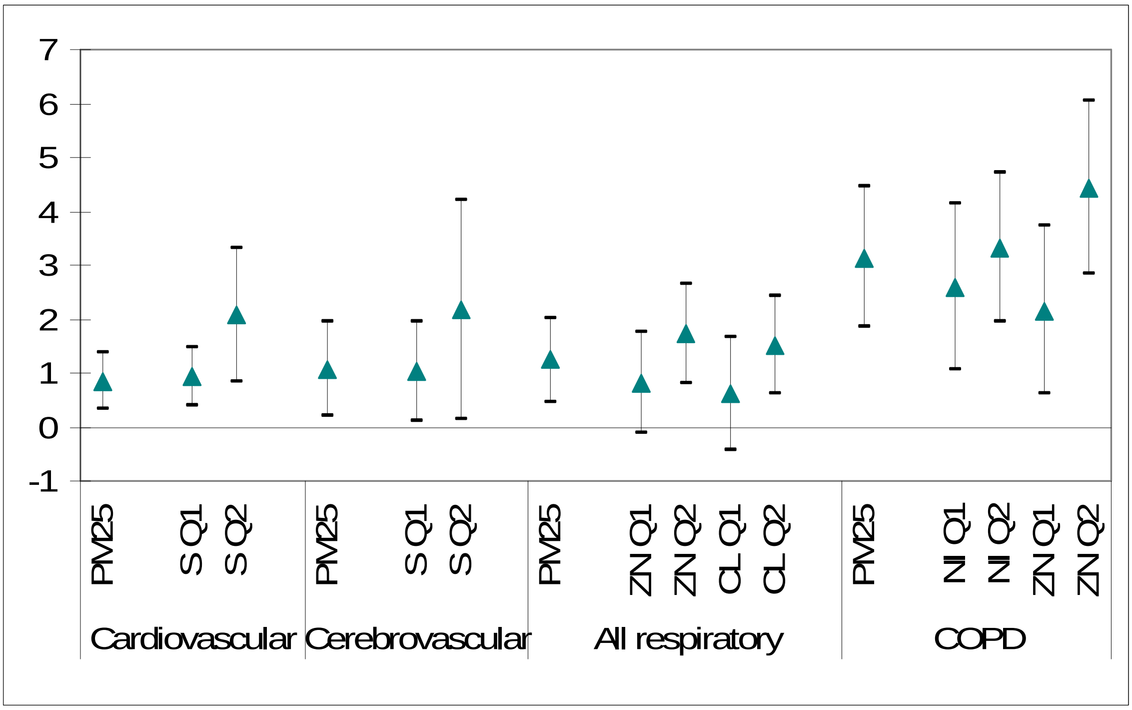
Component	Percentile				
	5th	25th	50th	75th	95th
Al	0.49	1.61	3.35	6.84	13.2
Na	0.42	2.23	6.53	15.1	28.8
Si	1.86	4.56	9.18	17.4	30.8
S	10.4	23.2	37.4	53.3	80.4
Cl	0.14	0.68	2.08	5.24	15.6
K	3.49	5.87	8.33	12.3	23.8
Ca	0.90	2.30	3.95	5.95	9.50
Cr	0.03	0.06	0.10	0.15	0.26
Mn	0.13	0.28	0.43	0.62	1.02
Fe	2.64	6.12	8.94	12.2	18.9
Ni	0.01	0.02	0.03	0.05	0.09
Cu	0.25	0.55	0.78	1.10	1.90
Zn	0.75	1.38	2.07	2.88	4.98
Se	0.01	0.04	0.07	0.15	0.31
Br	0.10	0.22	0.34	0.79	2.51
Pb	0.36	0.71	1.16	3.44	9.34

Table 3. The percent increase (95% Confidence Interval) in cause-specific mortality per 10 µg/m^3 increase in PM2.5.

Cause of death	% Increase	95% CI	
Cardiovascular	0.85	0.33	1.38
Cerebrovascular	1.07	0.20	1.94
All respiratory	1.24	0.45	2.03
COPD	3.14	1.85	4.45

Figures

Figure 1. Percent increase (95% Confidence Interval) in cause-specific mortality per 10 µg/m^3 increase in PM2.5 alone, and for the 1st and 3rd quartiles increase in the elements after including the interaction between PM2.5 and the mean monthly concentration ratios of species in the total PM2.5 mass.



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