Assessment of PM10 and heavy metals concentration in a Ceramic Cluster (NE Spain) and the influence on nearby soils.

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Abstract

Environmental pollution control is one of the most important goals in pollution risk assessment today. The aim of this study is conducting a retrospective view of the evolution of matter particulate (PM10) and the heavy metals (Cd, Ni and Pb) at different localities (Alcora, Castellón and Onda) in the Spanish cluster ceramic in a period between January 2007 and December 2011. The study area is in the province of Castellón. This province is a strategic area in the framework of European Union Pollution control. Approximately 80% of European ceramic tiles and ceramic frits manufacturers are concentrated in two areas, forming the so-called "Ceramics Clusters"; one is in Modena (Italy) and the other in Castellón (Spain). In these kind of areas, there are a lot of pollutants from this industry that represent an important contribution to soil contamination so it is necessary to control their air quality. In these areas atmospheric particles are deposited in the ground through both dry and wet deposition. Soil is a major sink for heavy metals released into the environment. For this purpose the levels of PM10 in ambient air and the corresponding annual and seasonal trend were calculated. The results of the study show that the PM10 and heavy metals concentrations are below the limit values recommended by European Union Legislation for the protection of human health and ecosystems in the study period. There is an important reduction of them from 2009 in all control stations due to economic crisis and subsequent decrease of industrial activity. The atmospheric seasonal tendency of pollutants concentrations is marked by the rate of industrial activity and additionally by the temperature. Complementary, a comparative study of heavy metals levels in soils was performed in this area. Soils with low pollution by Ni and Pb were detected, while different pollution by Cd was found depending on the sampling site. Although there is an evident reduction of PM10 and heavy metals levels, the results show that these pollutants have been accumulated in the soil close to emission sources.

Keywords: PM10, Heavy metals, soil pollution, ceramic cluster

1. Introduction

Environmental pollution control is nowadays one of the most important goals in pollution risk assessment. Metal contamination of the environment raises concern for the possible impact on human health, and the existence of heavy metals in soils, of both natural -inherited from the origin material (Galán et al., 2008), lithogenic or pedogenic; (Tume et al., 2011)- or anthropogenic origins -due to human activities as agricultural projects, water waste discharges or atmospherics emissions (Gray et al., 2003; Bech et al., 2008; Hovmand et al., 2008)-, is well-recognized as a potentially important source of human exposure (Muller and Anke, 1994; Davis et al., 2009; Chen et al., 2005).

PM10 particles and heavy metals are emitted into the atmosphere as aerosols, mainly as a result of human activities, and are deposited on the ground (Borgna et al., 2009). So the deposition of atmospheric particles is an important source of soil contamination in areas exposed to significant pollution levels. Sakagami et al. (1982) reported that there was a close relationship between heavy metal concentration in soils and those in the airborne particles that fall. Other authors have found that atmospheric inputs of heavy metals to agricultural systems can be a significant contribution to metal loading in soils. For example, Alloway. (1999) found a mean atmospheric deposition rate for Cd of around 1.9 g $ha^{-1}y^{-1}$, which Nicholson et al. (1999) calculated to be 50% of the total annual input of Cd to agricultural land in the UK. Nicholson et al. (1999) also calculated that atmospheric deposition of other metals such as Ni to be between 32-45% of the total annual inputs of these metals to soils. Then, in comparison to the other forms of metals inputs, potentially, atmospheric inputs have much more immediate impact on agricultural systems (Gray et al., 2003).

Once contaminated, soils typically remain in this condition for protracted periods of time because of sorption of metals on to particles and limited mobility (Peris et al., 2008; Ferri et al., 2012). This fact produces a potential human cumulative exposure. The accumulation of heavy metals in agricultural soils, including home vegetables gardens may be of particular concern since consumption of vegetable grown in metal contaminated soils may pose health risks for the population residing in these areas (Cui et al., 2005; Intawongse and Dean, 2006). Elevated concentrations of trace elements in the soil–water–plant ecological system are of great concern because of possible influences on the food chain. (Tume et al., 2008). While essential trace metals, such as Ni, are necessary for plant growth and/or human nutrition at low levels, they may also be toxic to both animals and humans at high exposure. Other trace elements, for example Cd and Pb, may also inadvertently enter the food chain and pose health risks to human and animals (Laughlin et al., 1999, Micó et al., 2006). Prolonged metal exposure spanning neurodevelopmental periods may also increase the risk of neurodegenerative conditions for elderly people (Aelion et al., 2008). Moreover, heavy metals in soils can generate airborne particles which may affect the air environmental quality (Gray et al., 2003).

The aim of this study is conducting a retrospective view of the evolution of particulate matter (PM10) and selected heavy metals (Cd, Ni and Pb) at different localities (Castellón, Alcora and Onda, fig.1) in the Spanish cluster ceramic from January 2007 to December 2011. Complementary, a comparative study of heavy metals levels in soils was performed in this area. The data were extracted from the papers of Roca-Pérez et al., (2010) and Jordán et al., (2009).

2. Description of the study area

The study area is located in the East of Spain, in the province of Castellón. This province is a strategic area in the frame work of the European Union (EU) pollution control. Approximately 80% of European ceramic tiles and ceramic frit manufacturers are concentrated only in two areas, forming the so-called "ceramics clusters"; one is in Modena (Italy) and the other in Castellón.

The type of climate in the study area is Mediterranean characterized by wet and mild winters, dry and warm summers, and an average temperature variation of 13.5ºC. Rainfall is abundant in spring and autumn, coinciding with the dominance of western winds while summer is drier, dominated by the Azores anticyclone (Vicente et al., 2011). Yearly rainfall generally does not exceed 400 mm.

This area has a complex Mediterranean atmospheric environment, with low rainfall, soil with poor vegetation coverage and frequent high particulate air-mass intrusions from the Sahara (Rodríguez *et al*., 2002). A system of local sea breezes is also present in the study area due to geographical characteristics and the proximity to the sea. These periodic land-sea winds, which have been extensively studied by several authors (Martín et al., 1991; Boix *et al*., 1995; Millán *et al*., 2001; Sanfeliu et al., 2002), govern the microclimate in this area, resulting in an overall effect of smoothing the temperatures (Pogosyan, 1965). Due to this system of breezes, the concentration of pollutants may be affected by emission sources located outside the study area on a daily basis (Fig. 1).

The origin of air PM10 in this area is both natural and anthropogenic. The former is due to the resuspension of mineral materials from the surrounding mountains with poor vegetation coverage and the long-range transport of materials from North Africa (Rodríguez *et al*. 2001, Pérez *et al*. 2006; Esteve *et al.* 2012). These dust intrusions from North Africa influence ambient PM10 levels in the study area at around 2 μ/m^3 on an annual basis (Minguillón *et al*, 2009).

Anthropogenic pollution sources originate from automobile traffic (mobile sources) and industrial activity (fixed sources). The main industrial activity in the study area is based on producing ceramic tile (Vicente *et al*. 2007). This industrial sector has two types of factories, one for the manufacture of tiles and the other to supply raw materials. The raw materials of the tile body consist mainly of clay from sources such as opencast quarries within the ceramic cluster area (Jordán *et al*., 2009; Sanfeliu *et al*., 2009). The raw materials for decoration involve manufacture frits, enamels, and colour (Jordán *et al.,* 2006). In the manufacture of ceramic tile, channelled and diffuse emissions from the production processes and the storage, handling and transport of raw materials all increase the concentration of particles in the air (Sanfeliu *et al*., 2002). However, particle emissions from the manufacture of pigments, frits and enamels probably have a greater impact on the levels of heavy metals than on particle mass. (Minguillón *et al*., 2007). An additional important factor is that a power station, a refinery and several chemical industries are located at east of the study area (Boix *et al*., 2001) (Fig. 1). These industries together contribute to environmental pollution in the area. Finally, relevant sources of secondary PM in the area include precursor emissions of the volatile organic compounds (VOC's), NOx and SO_2 from high temperature ceramic processes, power generation, petrochemical processes and biomass combustion (Minguillón *et al.*, 2007).

In the case of chemical pollutants in air PM10, nickel is found as a trace element in petrol, and therefore its release into the atmosphere is related mainly to the combustion of fossil fuels (coal and fuel oil) in electricity and heat production and also in traffic exhausts (Pacyna et al. 1984; Ghio and Samet 1999). Nickel oxides are also widely used as components of pigments used in the ceramics industry. Concentration levels of cadmium in ambient air are associated with industrial processes in the manufacturing of frits and enamel. Emissions of cadmium are also produced in the processes of a nearby power station (Boix et al. 2001). The most important emission of lead are traffic exhausts. Petrol additives contain lead (Parekh et al. 2002), which after combustion is released into the atmosphere as organic lead (lead bromide and lead chlorinebromide) (Pacyna 1998). With the introduction of new international laws, the use of lead in petrol has been banned, and this contribution is now minimal, its use reduced to obsolete means of transportation. In the ceramics industry, lead oxides are also used extensively as a component of pigments. Relationships between the emissions from this sector to air ambient levels of lead in close urban areas have been identified (Sanfeliu et al. 2002; Gómez et al. 2005).

The study is focused on 154 km^2 that is the surface between the three cities studied. Alcora is situated at 279 m above sea level, Onda at 194 m and Castellón at 30 m. There is a high altitude difference between these cities in a small area. The distance between Castellón, Alcora and Onda is 17 km.

The study area is based on Quaternary materials generated by torrents from inland massifs (Maestrazgo Range and tributaries from the Sierra de Espadán range), which have formed lagoons closer to the sea. This process is reported to have started at the end of the Tertiary period, as the Pliocene became the Pleistocene era, favoring a climate suitable for torrential erosion and subsequent transport and deposition. The main source of sediments has decreased in the last few years because of regulations of the course of the river (Vicente et al., 2007)

Alcora is in the Miocene surrounded by Cretaceous and Quaternary. Its materials are conglomerates, limestone, marl, clay and lignite. The materials around this city are limestone, marl, sand, clay and gravel. Onda is located in the Quaternary enclave, surrounding a Jurassic area. This town is surrounded by Quaternary and Triassic. The main materials of this city are conglomerates, limestones and dolomites, around marl, clay and limestone in the Triassic and red clays in the Quaternary. Castellón is located in the Quaternary and the main materials are clays, silts and sands. All deposits are Quaternary sedimentary.

3. Materials and Methods

3.1. Atmospheric particles

Sampling collection

A PM10 medium volume sampler model IND-LVS3 manufactured by Kleinfiltergerät was used. This device is considered as a reference according to European regulations (European Council Directive 2008/50/EC; UNE-EN 12341:1999), for the sampling of PM10 particles. The technology used in the equipment consists of blowing air through an inlet with a vacuum pump. The particulate matter was blown in through the opening circumference between the frame and the round cover mounted on top. Within the sampler inlet the airflow was accelerated by eight impactor nozzles and then directed toward the impacting surface. Particles were trapped on a permeable support consisting of a 47 mm diameter filter. The device contains a temperature sensor with a radiation protector that eliminates deviations in the reading caused by solar radiation in addition to a pressure sensor. The sampling flow volume was 2,3 m^3/h during 24 h periods. A total of 4.100 PM10 samples (1.496 Castellón, 1.253 Alcora and 1.351 Onda) were collected in filters from 2007 to 2010. The filters used were quartz fiber filters were used, according to UNE-EN 12341:1999. They were made from SiO_2 pure base, totally free of additives. These filters allow an efficiency of separation greater than 99.5%.

The samplers of the PM10 were positioned between 1,5 and 4m about the ground according to the Directive 2008/50/EC (Annex III, Microscale sitting of sampling points).

Gravimetric analysis

Particle concentrations levels were determined gravimetrically. This method consists of weighting the filters twice: firstly empty and then with sample**.** The filters must be kept for at least 48h in a special chamber. The conditions inside the chamber are 50% relative humidity and a temperature of 20ºC, according to normative UNE–EN 12341:1999. Filters were weighted on an analytical balance with a precision of 0.1 mg. The PM concentration levels were determined based on the sample quantities obtained and the volume of air pumped.

Chemical analysis

The levels of Cd, Ni and Pb in the PM10 samples were determined by inductively coupled plasma mass spectrometry (ICP-MS). The equipment used was an Agilent model 7500CX that included a quadrupole, a collision cell and an integrated autosampler. The equipment was installed in a chamber with a clean air filter unit and an independent air conditioning system. This instrumental technique allows the Cd, Ni and Pb levels to be rapidly identified after dissolution of the sample. Dissolution was achieved by acid digestion in hermetic Teflon recipients. This methodology has been used by many authors (Kubilay and Saydam, 1995; Querol *et al*., 2000).

In order to detect any possible traces of contamination-causing As, Cd, Ni or Pb contained in the reagents and quartz filter fibres, digestions with only reagents (blank reagents) and filters without a sample (blank filters) were performed. The SRM 1648 "urban particulate matter" pattern was used to validate the results. This pattern consists of particulate matter of anthropogenic origin collected in an industrialised urban atmosphere and was an adequate standard of reference for this study.

3.2. Soil

Sampling collection

The sampled soils were selected between the different samples from the papers of Roca-Pérez et al., (2010) and Jordán et al., (2009). The soils were chosen for their proximity of the industrial atmospheric emission sources and their physicochemical property diversities, especially pH (between 6.5 and 8) and carbonate content, the soil of Alcora is noncalcareous while Castellon and Onda are calcareous. In Alcora, almond trees are the main crop, followed by olive trees, vineyards, some carob trees, and a few fig trees.

In Castellón and Onda, the crop of orange trees is the main. These soils have a low capacity use and a erosion risk. In addition in Onda, there are other terraced fields destined for the cultivation of carob, olive, hazel and almond trees. All studied soils are anthrosols, according to the FAO World Reference Base for Soil Resources. These soils are a type formed or heavily modified due to long-term human activity, such as from irrigation, addition of organic waste or wet-field cultivation used to create paddy fields.

According to the soil classification of FAO/UNESCO 1998, the soils chosen of the papers of Roca-Pérez et al., (2010) and Jordán et al., (2009) are classified as:

- *Fluviosols:* Alcora and Castellón. Typical soils found of valley bottoms and floodplains, widely represented in the province of Castellón. These occupy the coastal plains and the terraces of the river courses from the inland areas to the coast. However, inland areas may develop on slopes fitted out by terraces. These soils are partly immature and they are commonly well drained. Because of their development from recent alluvial deposits, these soils have a significant thickness and a variable texture (Antolín Tomás, 1998).
- *Calcisol:* Onda. These types of soils are characterized by horizons with secondary enrichment of calcium carbonate, favored by semi-arid conditions. They are present either in the coastal plain or in the mountainous interior. In these soils predominate washing and carbonate accumulation is associated with geomorphic processes of glacis formation, alluvial fan, etc. (Antolín Tomás, 1998).

These authors collected two kilograms of topsoil samples (0-20 cm) from each sampling site, air-dried, crushed, 2 mm sieved, mixed and stored at air-dried conditions for further analysis.

Chemical analysis

The methodology used in soil chemical analysis was described by Roca-Pérez *et al.* (2010) and Jordán et al. (2009) in their studies. Total contents of metals were determined by ICP-MS after microwave digestion of 0.5g of representative soil sample using 9 ml nitric acid (68% w/v), 1 ml hydrogen peroxide (30% w/v), 3 ml hydrofluoric acid (48% w/v), 2 ml hydrochloric acid (37% w/v) and 5 ml deionised water in the first steps (20 min at 200ºC) and 30ml boric acid (4%) in the second (5min at 170ºC) (EPA, 1996).

4. Results and discussion

4.1. Atmospheric concentrations of pollutants.

Table 1 shows the assessment of PM10, Cd, Ni and Pb according the limit values established by European Legislation (European Council Directive, 2008/50/EC). The concentrations of the pollutants are below the limit values recommended by European Union Legislation for the protection of human health and ecosystems in the study period, with the exception of daily exceedances of PM10 in 2007 in the station of Castellón.

There is an important reduction of the pollutants from 2009 in all control station due to the economic crisis and subsequent decrease of industrial activity. Additionally, due to the new European Directive (2010/75/EU) on industrial emissions, the best available techniques (BAT) were implemented in the industry in order to prevent or reduce harmful impacts.

In Modena ceramic cluster this reduction has been also observed despite the Italian ceramic industry was the first in Europe to develop and adopt techniques for the reduction of the environment impacts in the seventies (Minguillón et al., 2013). So the economic crisis has been very important in the two industrial sites.

4.1.1 PM10

In general, PM10 levels increase during the months with high temperatures due to a decrease in precipitation (Fig. 2) with the exception of 2007 and 2008 in Castellón and Alcora. This causes a reduction in the cleansing effect on the atmosphere (Bergametti *et al*. 1989) and consequently a greater contaminant concentration in the ambient air. The high temperatures during these months lead to increased dryness of the terrain, which favours the resuspension of clay-loam substrate in the area (Gómez *et al*., 2005). At the same time, the mixing layer, or lower part of the troposphere where the pollutants are free to move through the turbulence generated in the lower layers of the atmosphere, increases its thickness and facilitates the mixing of air masses from the North of Africa in the low layers (Kubilay and Saydam, 1995). Intrusion episodes of long-distance material occur, leading to an increase in the concentration of PM10. During winter months, temperature inversions are generated. This phenomenon occurs on clear nights, with weak or no wind, when the soil losses the heat acquired by radiation and low-lying air layers are cooled faster than the upper layers of air (Wallace *et al*., 2010). When pollutants are emitted under temperature inversion conditions, they accumulate in the layers of the troposphere close to the ground. This phenomenon causes transport through these layers to occur too slowly, producing an increased concentration of pollutants (Monn et al., 1995). This accumulation of pollutants is also found in Milan due to persistent thermal inversions (Marcazzan *et al*, 2001). During the autumn season, the lowest values of the study were detected (Fig. 2). This was due to atmospheric instability, the tendency of the atmosphere to resist or enhance vertical motion or, alternatively, to suppress or augment existing turbulence (Zoras *et al*., 2006). According to some studies, as global weather conditions change, the input frequency of air masses from North Africa is reduced (the mixed layer decreases), rainfall increases, and there is a greater cleansing effect in the atmosphere (Querol *et al*., 2002, 2004).

The seasonal evolution of the pollutants concentrations could supply valuable information about the potential origin of them. These seasonal variations are dominated by changes in meteorological conditions (Chang and Lee, 2008) and by human activities (Guangjian et al., 2009).

4.1.2. Heavy Metals

The constant tendency of de cadmium concentration during the year (Fig. 3) indicates that the contribution of this pollutant into the atmosphere is continuous from all sources, both natural and anthropogenic. The small variation is due to one of the principal origins of cadmium in the study area, the use of this element in the form of oxide in the formulation of enamels and pigments in the ceramic industry (Matthes 1985). This sector cuts its production levels in the summer months and so cadmium levels were accordingly lower. In addition, the power plant located within the study area also emits cadmium (Boix et al. 2001), which is higher in the months of higher energy demand (cold months), wherein a light cadmium concentration increase was observed.

The light seasonal tendency for nickel (Fig. 4) of high concentrations during hot months and low ones during the coldest months leads to nickel concentration levels being governed by two factors: anthropogenic activities within the study area and the ambient temperature. High-temperature anthropogenic activities at the power and petrochemical plants, etc., release nickel into the atmosphere mainly as fly ash and not in a gaseous state (Boix et al. 2001). Due to their characteristics, these fine particles behave in the atmosphere like a gaseous pollutant (Wark and Warner, 2000), and so their dispersion is influenced by external factors like the temperature (Vicente et al., 2011). Higher temperatures result in greater atmospheric turbulence (Wark and Warner, 2000), bringing greater dispersion away from the emitting sources located to the east of the study area. The power and petrochemical plants are located there, thus favoring the enrichment of nickel in the particle concentration levels in farther-away zones during the hottest months.

The general behavior of lead concentration (Fig. 5) is to reach high levels in colder seasons and low levels during warmer seasons. In the study area, the origin is linked to the use of lead in the formulation of raw materials in the ceramic sector (Matthes 1985). These oxides are volatized in high-temperature industrial processes and they condense upon contact with the atmosphere. An aerosol–vapor equilibrium exists for lead dependent upon the air temperature. Low temperatures favor the aerosol phase, while high temperatures favor the vapor phase release, explaining that the dispersion is greater at high temperatures, and therefore lead levels are less in areas near the emitting sources. Dispersion is less at low temperatures and so greater concentrations of this contaminant abound near the emitting sources (Vicente et al., 2011). Another factor needing consideration is that, in summer, this sector reduces production during vacation periods, resulting in less emissions and lower lead concentration levels in the ambient air.

4.2 Soil pollution.

Heavy metal concentrations in some different environments show high variability depending on the type of environment (industrial, urban or natural). Some authors have conducted studies of soils in different environments (Galán et al., 2002; Moral et al., 2005; Tong-Bing et al., 2005; Yay et al., 2008; Maas et al., 2010) and concluded that the soils most polluted by heavy metals occur in areas affected by mining and cement factories (Soriano et al., 2012).

Soils affected by heavy metal emissions and PM10 in the ceramic cluster are carbonate reliefs, detrital or gypsiferous materials subsequently colluvial-alluvial deposits and marsh. The presence of carbonate indicates high soil pH, which tends to precipitate the heavy metals. The Cd, and other metals have a strong tendency to be adsorbed by carbonates. The Cd mobility is medium in basic and neutral soils, low in Pb and very low in Ni (García et al., 2009).

Table 2 shows classification of soil contamination types based on their heavy metals concentrations, with four categories identified.

Table 3 shows heavy metals concentration in soil in the study area. According to the polluted soil classification (table 2), in Onda and Alcora, the soils show no pollution by nickel but in Castellón shows light pollution. In the case of cadmium, Onda has light pollution, Alcora medium and in Castellón very extreme pollution was detected. The soils from Alcora and Castellón are unpolluted by lead and Onda shows medium pollution.

According to studies by D'Elia et al., (1999) the soils of the Bologna area have standard values of lead as in Castellón and Alcora, low pollution of cadmium as in Onda, while medium pollution of nickel were detected.

5. Conclusions

In this study a retrospective view of evolution of PM10 and the heavy metals (Cd, Ni and Pb) was conducted at three cities in the Spanish ceramic cluster, from 2007 to 2011. The results show that the concentrations of studied pollutants are below the limit values of European laws for the protections of human health and ecosystems, with the exception of daily exceedances of PM10 in 2007 in the station of Castellón. An important reduction of the pollutants from 2009 in all control station are detected due to the economic crisis and subsequent decrease of industrial activity

The atmospheric seasonal tendency of the pollutant concentrations in the study area is marked by the rate of industrial activity and, additionally, by the ambient temperature.

Additionally, a comparative study of heavy metals in soils was performed in this area because although the particle deposition process cleans the atmosphere, its ultimate result is the transfer of toxic atmospheric pollutants into the soil. The study of metals contents in soil is currently necessary to obtain reference values and assess their contamination, because the pollution from atmospheric particulate metals in the soil increases their toxicity

Soils with low pollution by nickel and lead were detected in the study area, while different pollution by cadmium was found depending on the sampling site, Castellón shows extreme pollution, Alcora medium and Onda low.

Even if there is an evident reduction of PM10 and heavy metals atmospheric levels in the study area, these pollutants have been accumulated in the soil close to emission sources for years. The persistence of these pollutants in soil is much longer than in other compartments of the biosphere, especially heavy metals which can be considered virtually permanent. So, it is very important to know and reduce the emissions in order to minimize harmful effects on human health, with particular attention to sensitive populations, and diminish damage to the environment as a whole. In this paper, the importance of soil composition has been identified to develop environmental control strategies

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References

Aelion, C.M., Davis, H.T., McDermott, S., Lawson, A.B. 2008. Metal concentrations in rural topsoil in South Carolina: potential for human impact. Science of the Total Environment 402,149-156.

Antolín Tomás, C. 1998. El suelo como recurso natural en la Comunidad Valenciana. Generalitat Valenciana. Valencia, Spain.

Alloway, BJ. 1999. Atmospheric deposition of heavy metals onto agricultural land in England and Wales. In: Wenzel WW, Adriano DC, Alloway B, Doner HE, Keller C, Lepp NW, Mench M, Naidu R, Pierzynski GM, editors. Fifth International Conference on the Biogeochemistry of Trace Metals, 11–15 July 1999, Vienna, Austria. 1, 414–415

Bech, J., Tume, P., Sokolovska, M., Reverte, F., Sánchez, P., Longan, L., Bech, J., Puente, A., Oliver, T. 2008. Pedogeochemical mapping of Cr, Ni, and Cu in soils of the Barcelona Province (Catalonia, Spain): Relationships with soil physico-chemical characteristics. Journal of Geochemical Exploration 96, 106–116.

Bergametti, G., Dutot, A.L., Buat-Menard, P., Losno P., Remoudaki, E., 1989. Seasonal variability of the elemental composition of atmospheric aerosol particles over the Nortwestern Mediterranean. Tellus 41B, 353-361.

Boix A., Jordán M.M., Querol X., Sanfeliu T., 2001. Characterization of total suspended particles around a power station in an urban coastal area in eastern Spain. Environmental Geology 40, 891-896.

Borgna, L., Di Lella, L.A., Nannoni, F., Pisani, A., Pizzetti, E., Protano, G., Riccobono, F., Rossi, S. 2009. The high contents of lead in soils of northern Kosovo. Journal of Geochemical Exploration 101, 137-146.

Chang, S.C. and Lee, C.T. 2008. Evaluation of the temporal variations of air quality in Taipei city, Taiwan, form 1994 to 2003. Journal of Environmental Management 86, 627-635.

Chen, T., Zheng, Y., Lei, M., Huang Z., Wu, H., Chen, H., Fan, K., Yu, K., Wu, X., Tian, Q. 2005. Assessement of heavy metal pollution in surface of urban parks in Beijing, China. Chemosphere 60,542-551

Cui, Y., Zhu, Y.G., Zhai, R., Huang, Y., Qiu, Y., Liang, J. 2005. Exposure to metal mixtures and human health impacts in a contaminated area in Nanning, China. Environmental International 31,784-790.

Davis, H.T., Aelion, C.M., McDermott, S., Lawson, A.B. 2009. Identifying natural and anthropogenic sources of metals in urban and rural soils using GIS-Based data, PCA, and spatial interpolation. Environmental Pollution 157, 2378-1385

D'Elia, V., Lodi, V., Naldi, M., Gherardi, G., Violante, F.S., Bonparola, M., Badiello, R., Raffi, G.B. 1999. Gardening work and heavy metals in urban environment. Archives of Industrial Hygiene and Toxicology. 50:163-170.

EPA, 1996. Method 3052. Microwave assisted acid digestion of siliceous and organically based matrices. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency response, Washington, D.C. http://www.epa.gov/epaoswer /hazwaste/test/pdfs/3052.pdf.

European Council Directive 2008/50/EC of 21st May 2008 on ambient air quality and cleaner air for Europe. Official Journal of the European Union L152, 11th June, 2008, 1-44.

European Council Directive 2010/75/EC of 24th November 2010 on industrial emissions (integrated pollution prevention and control). Official Journal of the European Union L1334, 17th December, 2010, 17-119.

Esteve, A.R., Estellés, V., Segura, S., Utrillas, M.P., Martínez-Lozano, J.A. 2012. Influence of the trajectory of air masses on the in situ measurements of aerosol properties in Valencia. Tethys 9: 35-41.

FAO/UNESCO, 1998. World reference base for soil resources. 84 World soil resources reports. International Society of Soil Science, Rome.

Ferri, R., Donna, F., Smith, D.R., Guazzetti, S., Zacco, A., Rizzo, L., Bontempi, E., Zimmerman, N.J., Lucchini, R. 2012. Heavy metals in soil and salad in the proximity of Historical ferroalloy emission. Journal of Environmental Protection 3, 374-385.

Galán, E., González, I., Fernández-Caliani, J.C., 2002. Residual pollution load of soils impacted by the Aznalcóllar (Spain) mining spill after clean-up operations. The Science of the Total Environment 286, 167 – 179.

Galán, E., Fernández-Caliani, J.C., Gónzalez, I., Aparicio, P., Romero, A. 2008. Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South–West Spain. Journal of Geochemical Exploration 98, 89–106

García, I., Díez, M., Martí, N., Simón, M., Dorronsoro, C. 2009. Mobility of arsenic and heavy metlas ins a sandy-loam textured and carbonated soil. Pedosphere, 19 (2),166-175

Ghio, A.J. and Samet, J.M. (1999) “Metals and air pollution particles”. En: Air pollution and health. Eds. Holgate S.T.; Samet J.M.; Koren H.S.; Maynard R.L. Ed. Academic Press. pp.634-651.

Gray, C.W., McLaren, R.G., Roberts, A.H.C. 2003 Atmospheric accessions of heavy metals to some New Zealand pastoral soils. The Science of the Total Environment 305, 105-115.

Gómez, E.T., Sanfeliu, T., Jordán, M.M., Rius, J., 2005. Evolution, sources and distribution of mineral particles and amorphous phase of atmospheric aerosol in an industrial and Mediterranean coastal area. Water, air, and soil pollution 167, 311-330.

Guangjian, W., Baiqing, X., Tandong, Y., Chenglong, Z., Shaopeng, G. 2009. Heavy metals in aerosol samples from the Eastern Pamirs collected 2004–2006. Atmospheric Research 93, 784–792.

Hovmand, M.F., Kemp, K., Johnsen, I., Riis-Nielsen, T., Pacyna, J.M. 2008. Atmospheric heavy metal deposition accumulated in rural forest soils of southern Scandinavia. Environmental Pollution 155, 537-541.

Intawongse, M. and Dean, J:R. 2006. Uptake of heavy metals by vegetables plants grown on contaminated soil and their bioavailability in the human gastrointestinal tract. Food Additives & Contaminants 23, 36-48.

Jordán M.M, Álvarez C., Sanfeliu T., 2006. Spherical particles as tracers of atmospheric ceramic industry. Environmental Geology 51, 447–453.

Jordán, M.M., Montero, M.A., Pina, S., García-Sánchez, E., 2009. Mineralogy and distribution of Cd, Ni, Cr, and Pb in Biosolids-Amended Soils From Castellón Province (NE Spain). Soil Science 174 (1), 1–7.

Kubilay, N. and Saydam, A.C., 1995. Trace elements in atmospheric particulate over the eastern Mediterranean; concentrations, sources and temporal variability. Atmospheric Environment 29, 1352-1310.

Laughlin, M.J., Parker, D.R., Clarke, M. 1999. Metals and micronutrients-food safety issues. Field Crops Research 60,143-163.

Maas, S., Scheifler, R., Benslama, M., Crini, N., Lucot, E., Brahmia, Z., Benyacoub, S., Giraudoux, P., 2010. Spatial distribution of heavy metal concentrations in urban, suburban and agricultural soils in a Mediterranean city of Algeria. Environmental Pollution 158, 2294–2301.

Marcazzan, G.M., Vaccaro, S., Valli, G., Vecchi, R., 2001. Characterization of PM2.5 and PM10 particulatte matter in the ambient air of Milan (Italy). Atmospheric Environment 35, 4639-4650.

Martín M.; Plazas J.; Andrés M.D., Bezares J.C. Millán M.M., 1991. Comparative study of seasonal air pollutant behaviour in a Mediterranean coastal site: Castellón (Spain)" Atmospheric Environment 25A, 1523-1535.

Matthes, W. E. 1985. Vidriados cerámicos Ed. Omega. Madrid

Micó, C., Recatalá, L., Peris, M., Sánchez, J. 2006. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. Chemosphere 65, 863–872.

Minguillón M.C., Querol X., Alastuey A., Monfort E., Mantilla E., Sanz M.J., Sanz F., Roig A., Renal A., Felis C., Miró J.V., Artiñano B., 2007. PM10 speciation and determination of air quality target levels. A case study in a highly industrialized area of Spain" Science of the total environment 372, 382-396.

Minguillón M.C., Monfort E., Querol X., Alastuey A., Celades I., Miró J.B., 2009. Effect of ceramic industrial particulate emisión control on key components of ambient PM10. Journal of Environmental Management 90, 2558-2567.

Minguillón, M.C., Monfort, E., Escrig, A., Celades, I., Guerra L., Busani, G., Sterni, A., Querol, X. 2013. Air quality comparison between two Euroopean ceramic tiles clusters. Atmospheric Environment 74,311-319.

Millán, M.M., Artiñano, B., Alonso, L., Navazo, M., Castro, M. 2001, The effect of meso-scale flows on regional and long-range atmospheric transport in the western Mediterranean area. Atmospheric Environment 25, 946-963

Monn, Ch., Braenli, O., Schaeppi, G., Schindler, Ch., Ackermann-Liebrich, U., Leuenberger, Ph. and Sapaldian Team, 1995. ·Particulate matter <10 μm (PM10) and total suspended particulate (TPS) in urban rural and alpine air in Switzerland. Atmospheric Environment 29, 2565-2573.

Moral, R., Gilkes, R.J., Jordán, M.M., 2005. Distribution of heavy metals in calcareous and non-calcareous soils in Spain. Water, Air and Soil Pollution 162, 127 ‒ 142.

Muller, M and Anke, M. 1994. Distribution of cadmium in the food chain (soil-plant-human) of a cadmium exposed area and the health risks of the general population. Science of the total environment 156, 151-159

Nicholson, F.A., Alloway, B,J,, Carlton-Smith, C. 1999.Sources of heavy metals to agricultural soils in England and Wales. In: Wenzel WW, Adriano DC, Alloway B, Doner HE, Keller C, Lepp NW, Mench M, Naidu R, Pierzynski GM, editors. Fifth International Conference on the Biogeochemistry of Trace Metals, 11–15 July 1999, Vienna, Austria. 1:264–265

Pacyna J.M.; Semb A.; Hanssen J.E. 1984. Emission and long-range transport of trace elements in Europe. Tellus 36B,163-178.

Pacyna J.M. 1998. Sources inventories for atmospheric trace metals. In: Atmospheric particles. IUPAC Series on analytical and physical chemistry of environmental systems. Eds. Harrison R.M.; Van Grieken R:E. Ed. J. Wiley & Sons Vol.5:385-424.

Parekh P.P., Khwaja H.A., Khan A.R., Naqvi R.R. 2002. Lead content of petrol and diesel and its assessment in an urban environment. Environmental Monitoring and Assessment 74,255-262.

Pérez, C., Nickovic, S., Baldasano, J.M., Sicard, M., Rocadenbosch, R., 2006. A long Saharan dust event over the western Mediterranean: Lidar sun photometer observations, and regional dust modeling. Journal of Geophysical Research Vol. 111, D15214 doi: 10.1029/2055JD006579.

Peris, M., Recatalá, L., Micó, C., Sánchez, R. 2008. Increasing the Knowledge of Heavy Metal Contents and Sources in Agricultural Soils of the European Mediterranean Region. Water, Air and Soil Pollution 192:25–37.

Pogosyan K.H.P., 1965. The air envelope of the earth. Published by The Israel program for scientific translations. Jerusalem, Israel.

Querol, X., Alastuey, A., López-Soler, A., Plana, F., 2000. Levels and chemistry of atmospheric particulates induced by spill of heavy metal mining wastes in the Doñana area Southwest, Spain. Atmospheric Environment 34, 239-253.

Querol, X., Alastuey, A., Rosa, J., Sánchez-De-La-Campa, A., Plana, F., Ruir, C.R. 2002. Source apportionment analysis of atmospheric particles in an industrialised urban site in Southwestern Spain. Atmospheric Environment 36, 3113-3125.

Querol, X., Alastuey, A., Rodriguez, S., Viana, M.M., Artiñano, B., Salvador P., Mantilla, E., García de los Santos, S., Fernández Patier ,R., De la Rosa, J., Sánchez de la Campa, A., Mendendez, M. 2004. Levels of particulate matter in rural, urban and industrial sites in Spain. Science of the Total Environment 334-335:359-376

Roca-Pérez, L., Gil, C., Cervera, M.L., González, A., Ramos, J., Pons, V., Bech, J., Boluda, R., 2010. Selenium and heavy metals content in some Mediterranean soils. Journal of Geochemical Exploration. 107,110-116.

Rodríguez, S., Querol, X., Alastuey, A., Kallos, G., Kakaliagaou, O. 2001. Saharan dust contribution to PM10 and TPS levels in southern and eastern Spain. Atmospheric Environment 32, 2433-2447.

Rodríguez, S., Querol, X., Alastuey, Mantilla E., 2002. Origin of high summer PM10 and PST concentrations at rural sites in Eastern Spain. Atmospheric Environment 36, 3101-3112.

Sanfeliu T., Jordán M.M., Gómez E.T., Álvarez C., Montero M.A., 2002. Distribution of the atmospheric emissions of Spanish ceramics industries. Environmental Geology 41, 601-607.

Sanfeliu T., Jordán M.M., 2009. Geological and environmental management of ceramic clay quarries: a review. Environmental Geology 57, 1613–1618.

Sakagami, K.I., Eamada, R., Kurobe, T. 1982. Heavy metals contents in dust fall and soil of the National Park for Nature Study in Tokyo. Mitteilungen der Deutschen Bodenkundlichen Gessellscaft 33,59-66.

Soriano, A., Pallarés, S., Pardo, F., Vicente, A.B., Sanfeliu, T., Bech, J. 2012. Deposition of heavy metals from particulate setteable matter in soils of an industrialised area. Journal of Geochemical Exploration. 113, 36-44.

Tong-Bin, C., Yuan-Ming, Z., Mei, L., Ze-Chun, H., Hong-Tao, W., Huang, C., Ke-Ke, F., Ke, Y., Xiao, W., Qin-Zheng, T., 2005. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. Chemosphere 60, 542–551.

Tume, P., Bech, J., Tume, L., Bech J., Reverter F., Logan, Ll., Cendonya, P. 2008. Concentrations and distributions of Ba, Cr, Sr, V, Al, and Fe in Torrelles soil profiles (Catalonia, Spain). Journal of Geochemical Exploration 96, 94–105

Tume, P., Bech, J., Recerter, F., Bech, J., Longan, L., Tume, L., Sepúlvera, B. 2011. Concentration and distribution of twelve metals in Central Catalonia surface soils. Journal of Geochemical Exploration 109, 92-113.

UNE-EN 12341:1999 Air quality: Determination of the PM10 fraction of the suspended particulate matter. Reference method and field test procedure to demonstrate reference equivalence of measurement methods.

Vicente A.B., Jordan M.M., Pallarés S., Sanfeliu T., 2007. PM10 and Pb evolution in an industrial area of the Mediterranean basin. Environmental Geology 51, 1413-1424.

Vicente A.B., Sanfeliu T., Jordan M.M., 2011. Comparison between industrial-urban and rural particle stations in a ceramic cluster (NE, Spain). Water, Air and Soil Pollution 215, 83-96.

Wallace J., Corr D., Kanaroglou P., 2010. Topographic and spatial impacts of temperature inversions on air quality using mobile air pollution surveys. Science of The Total Environment 408, 5086-5096.

Wark, K., and Warner, C. F. 2000. Air pollution. Its origin and control Baldera, Mexico: Harper & Row. 99-137.

Yay, O., Alagha, O., Tuncel, G., 2008. Multivariate statistics to investigate metal contamination in surface soil. Journal of Environmental Management 86, 581–594

Zoras, S., Triantafyllou, A.G., Deligiorgi, D., 2006. Atmospheric stability and PM10 concentrations at far distance from elevated point sources in complex terrain: Worst-case episode study. Journal of Environmental Management 80, 295-302.