Inorganic geochemistry of roadway dust from the metropolitan area of Palermo, Italy

D. Varrica · G. Dongarrà · G. Sabatino · F. Monna

Abstract Inorganic matter from roadway dust collected in the urban area of Palermo, Italy, was analysed to identify the chemical elements introduced into the environment as a result of human activities. Metals of environmental concern exhibit very high enrichment factors, which in some cases exceed 100. Metal size distribution indicates that Pd, Pt, Au, Sb, Zn, S, Ni, V, Mo and Cr substantially accumulate in the finest particles, whereas Pb, Br, As, Cu, Ag and Ba are almost independent of the size fraction. SEM/EDS analyses revealed that some individual particles contain clusters of foreign particles (<10 μm) made up of Fe-Ni, Cr-Ni or Fe alone, typical of the abrasion of stainless steel. Others are aggregates of smaller Pb-Br-Cl particles. Lead isotope composition indicates that Pb pollution is mainly due to automobile exhausts and industrial sources. Pt and Pd concentrations reveal the increasing release of these elements into the environment from catalytic converters. Data indicate that monitoring Total Solid Particles, as generally done by the municipal agencies for the environment, is inadequate from a sanitary point of view, while there is a need for more attention to the presence of trace elements in airborne particulate matter and their distribution as a function of particle size.

Keywords Environmental pollution · Roadway dust · Heavy metals · PGE · Environmental geochemistry

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Introduction

There is much concern worldwide over the risk to human health posed by trace elements in ambient air and dust. Although heavy metals and metalloids are part of the environment, since they are natural constituents of the crust, their emissions from automobile exhausts and industry have modified the chemistry of the atmospheric aerosol, influencing the biogeochemical cycle of some elements. Therefore, people living in urban areas are exposed not only to conventional gaseous pollutants, but also to the hazardous trace elements, for which the risks to health are not always well assessed. Roadway dust, because of its composite origin, contains an amazing variety of toxic trace elements bound to particles of different sizes, which in turn are often related to their formation process. Consequently, the residence time of metals in air, independently of their origin, is closely related to the size of particles in which they are bound. While soil-derived metals are of little environmental concern because of their coarse particle sizes, smaller-sized heavy metals, which remain in suspension for days or even weeks, may have adverse health effects because of their ability to penetrate the respiratory system, ending up in lung capillaries and alveoli. Among the trace elements predominantly found in road dust and known to be hazardous to human health, lead is the toxic metal of greatest concern. However, in the last decade, because of the phasing-out of lead in gasoline, a continuous decrease in lead concentrations has been observed in airborne particulate matter, although still present (Aiuppa and others 2001). Unleaded gasoline was introduced in Europe during the late 1980s, when a new generation of cars were equipped with catalytic converters. Exploiting the catalytic properties of the noble metals platinum, palladium and rhodium (PGE), the converters reduce the emission of CO, not combusted hydrocarbons

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and NOx, favouring redox reactions and leading to the formation of less dangerous compounds (CO_2, N_2, H_2O). However, the introduction of catalytic converters is now causing a considerable rise in the concentration of these elements in several natural matrices such as soil, urban water and vegetation near areas subjected to intense vehicular traffic (Barefoot 1997; Helmers and others 1998; Schäfer and Puchelt 1998; Schäfer and others 1999; Zereini and Alt 2000). This paper discusses the composition of roadway dust collected in the urban area of Palermo, Italy, and aims to identify the chemical elements introduced into the environment by human activities. Two recent biogeochemical prospections (Alaimo and others 2000; Dongarrà and others 2003), carried out in the same area and using pine needles as bioaccumulators, showed the presence of heavy metals in the study area. While those data refer to an accumulation period of 2–3 years, the present work aims to highlight the presence of heavy metals and PGE in roadway dust over a shorter period of accumulation. The present report is part of an ongoing wider research program aimed at assessing the impact of natural and anthropogenic emissions of heavy metals in Sicily, the island being characterized by the presence of large cities, industrial zones, active volcanoes and rural areas. Earlier papers regarding this research project are: Dongarrà and others (1994, 2002); Dongarrà and Varrica (1998); Monna and others (1999); Aiuppa and others (2000, 2001); Alaimo and others (2000); Allard and others (2000); Varrica and others (2000).

Materials and methods

Study area

The study area is situated on the north-eastern coast of Sicily, and it is entirely covered by sedimentary rocks (limestones, clay, marly-clay and white or yellow quaternary biocalcarenites). Part of the eastern sector of the town is covered by a bright red-coloured soil, rich in Fe-oxides, known as 'Terra Rossa'. Palermo has a population of about 1 million inhabitants and it is a city where major industrial installations are lacking. The dominant natural sources of trace elements in air are wind-blown dust and sea spray. Potential local pollutants are limited to emission from vehicular traffic, house heating and small manufacturing industries.

Sampling method and analysis

A composite roadway dust sample was taken in Palermo in April 2000, after a dry period of 15 days, at different points, along a main street 3 km long, with high traffic density. The sampling sites were chosen as representative of one of the most polluted areas of the town. The dust sample was collected using a plastic brush and tray. A total of 1.5 kg sample was collected and stored in plastic bags. The sample was initially sieved through a 500-μm sieve to remove extraneous stones, pebbles and grass and then divided by particle diameter into five physical size fractions, 500–250, 250–125, 125–63 , 63-40 and <40 μm, using ASTM sieves. Particle composition and morphology were examined by X-ray diffraction, scanning electron microscopy (SEM) and electron probe microanalysis (EDS) using a SEM LEO 420 (University of Messina) and an SEM LEO 440 (University of Palermo). Major and trace elements in the five subfractions were analysed by INAA (Br, Ba, Co, Cr, Fe, Mo, Na, Sb, Sc, Hf, As, La, Ce, Nd, Sm, Yb, Lu) and ICP-MS (Al, Ca, Mg, P, Sr, Ti, K, Mn, Cu, Pb, Zn, Cd, S, Y, Ag, Ni, V) at Activation Laboratories Ltd. (Ontario, Canada). Standard reference materials from USGS were employed. The tested values were all >90% of the certified values. Several replicates yielded precision in the ranges 5–10% (major elements) and 20–30% (trace elements), respectively. Pt, Pd and Au were analysed at Activation Laboratory by the lead fire assay using Ag as a collector. About 30 g of urban road dust were mixed with fire assay fluxes and fused at 1,050 °C for 1 h. After cooling, the lead button was separated from the slag and cupelled at 1,000 °C to recover the Ag (doré bead) + Pt, Pd and Au. The Ag doré bead was digested in hot (95 °C) HNO_3 + HCl. After cooling, the sample solution was analysed for Pt and Pd by ICP/MS using a Perkin Elmer Sciex ELAN 6100 ICP/MS. UMT-1 and WMS-1 reference materials from CANMET were used. The detection limits were 3 ng/g for Pt and Pd and 1 ng/g for Au (Hoffman and Dunn 2002). The chemical composition of each subsample of the urban dust is presented in Table 1.

Lead isotope analysis

Lead isotope measurements were performed at the F.A. Forel Institute (Versoix, Switzerland). Each subsample was separated into a magnetic and non-magnetic fraction by a Frantz isodynamic magnetic separator. The sample preparation for isotope analysis was carried out under class 100–1000 laminar air flow clean benches in a clean room. About 100 mg of each dust sample was totally dissolved on a hot plate in a pressurised Teflon beaker (Savilex) using a mixture of 3 ml of each concentrated HF, HCl and HNO_3 Suprapur grade. Once dissolved, the solutions were evaporated and the lead was separated on ionic resin AG1X4 (Biorad) following the conventional technique (loading in 2 N HBr, washing with the same acid, and elution with 6 N HCl). Taken up in 1% (v/v) nitric acid, purified lead was measured by quadrupole-based ICP-MS (HP 4500). More details about the measurements, mass bias correction and preparation procedures can be found in Monna and others (1998; 2000). Total blank was checked and found totally negligible with respect to the amount contained in unknown samples. The obtained isotope data are given in Table 2.

Results

X-ray powder diffraction

The mineralogical characterization of the five subfractions of road dust revealed that, apart from the different abundance ratios, calcite, dolomite and quartz are the main minerals, thus indicating the presence of materials derived

Table 1
Chemicalcomposition of the urban roadway dust (data in mg/kg). * Pd, Pt and Au (µg/kg) have been measured by ICP-MS following lead fire assay. The analytical precision was in the range 5–10% for major elements and 20–30% for trace elements. Tested values of Standard Reference Material from USGS were all >90% of the certified values

	Ca (ICP-MS)	Mg (ICP-MS)	Al (ICP-MS)	Fe (INAA)	Ti (ICP-MS)	K (ICP-MS)	Na (INAA)	P (INAA)
Detection limit	100	100	100	100	100	100	100	10
500–250 mm	206,200	30,200	5,000	26,800	600	1,600	2,800	1,150
250–125 mm	170,600	22,100	6,000	25,200	900	1,800	3,500	1,100
125–63 mm	175,800	28,900	6,900	32,100	1,200	2,000	4,100	1,160
63–40 mm	177,800	31,800	9,300	32,300	1,500	2,600	1,900	1,300
<40 mm	183,400	30,900	12,000	26,600	1,900	3,300	1,800	1,470
	Ag (ICP-MS)	As (INAA)	Au*	Ba (INAA)	Br (INAA)	Cd (ICP-MS)	Ce (INAA)	Co (INAA)
Detection limit	0.3	0.5	1	50	0.5	0.3	3	1
500–250 mm	1.1	7.5	72	250	82.7	1.1	14	7
250–125 mm	0.9	7.9	164	510	64.9	0.8	19	6
125–63 mm	8.1	6.6	3,010	170	77.1	0.8	24	7
63–40 mm	4.6	7.2	3,360	240	71,5	1,1	28	7
<40 mm	5.5	6.2	5,930	330	63.4	2.1	35	7
	Cr (INAA)	Cu (ICP-MS)	Hf (INAA)	La (INAA)	Lu (INAA)	Mn (ICP-MS)	Mo (ICP-MS)	Nd (INAA)
Detection limit	2	1	1	0.5	0.05	1	1	5
500–250 mm	103	98	1	6.3	0.09	179	4	6
250–125 mm	118	574	2	7.2	0.08	197	6	5
125–63 mm	212	992	7	8.9	0.14	280	11	6
63–40 mm	240	652	7	12.8	0.21	316	12	8
<40 mm	203	536	7	16.2	0.22	309	15	12
	Ni (ICP-MS)	Pb (ICP-MS)	Pd*	Pt*	S (ICP-MS)	Sb (INAA)	Sc (INAA)	Sm (INAA)
Detection limit	1	3	0.1	0.1	100	0.1	0.1	0.1
500–250 mm	14	544	37	115	n.d.	16.2	1.5	1
250–125 mm	15	596	79	192	400	20.8	1.7	1.1
125–63 mm	30	755	260	395	600	26.2	1.9	1.4
63–40 mm	35	711	531	290	900	41.2	2.6	1.7
<40 mm	40	716	1,070	396	1,300	50.8	3	2.2
	Sr (ICP-MS)	V (ICP-MS)	Y (ICP-MS)	Yb (INAA)	Zn (ICP-MS)			
Detection limit	1	2	1	0.2	1			
500–250 mm	186	13	5	0.6	207			
250–125 mm	195	15	5	0.5	400			
125–63 mm	183	20	6	0.9	404			
63–40 mm	200	23	7	1.2	455			
<40 mm	211	28	8	1.4	485			

Table 2
Lead isotope ratios in magnetic (*A*) and non-magnetic (*B*) fractions; the errors are given at a 95% confidence level

Size		^{206}Pb/^{207}Pb	+/–	^{208}Pb/^{206}Pb	+/–
500–250	µm (A)	1,137	0.003	2,114	0.008
500–250	µm (B)	1,161	0.003	2,108	0.007
250–125	µm (A)	1,140	0.003	2,108	0.006
250–125	µm (B)	1,149	0.004	2,096	0.008
125–63	µm (A)	1,137	0.003	2,109	0.007
125–63	µm (B)	1,146	0.004	2,102	0.011
63–40	µm (A)	1,145	0.006	2,102	0.009
63–40	µm (B)	1,147	0.003	2,098	0.008
<40	µm (A)	1,144	0.003	2,108	0.007
<40	µm (B)	1,144	0.004	2,103	0.008

from the surrounding geological formations and probably from construction wear. In the same study area Alaimo and Ferla (1979), beside the above minerals, identified traces of palygorskite. This latter mineral has been occasionally found, and appears to be transported as dust from the Sahara desert. For our purposes, the low content of anthropogenic metals in Saharan dust has the effect of reducing the concentrations of anthropogenic trace metals in the collected particulate matter (Chester and others 1996).

SEM/EDS analyses

The 500–40-µm fraction

The following discussion deals with particles between 500 and 40 µm, thus grouped because of the substantial compositional homogeneity of the 500–250, 250–125, 125–63 and 63–40 µm size fractions. Such homogeneity is the expression of mechanically-generated aerosols from resuspension of soil dust. Particles belonging to this large group are irregularly shaped, sometimes rounded, and are mainly composed of calcite, dolomite, quartz and Al-silicates. Some of them, when observed by backscattered electron microscopy, show bright spots consisting of metal associations such as Sn-Cu, Fe-Cr, Ba-Zn-Fe and Fe-Br. Others are aggregates of smaller particles of Pb, Br and Cl.

The 40-µm fraction

SEM observation revealed three categories of particles, according to their approximate size: coarse (40–20 µm), medium (20–10 µm) and fine (<10 µm). Although the coarse particles, containing Ca, Mg, Si and Al, are essentially crustal, some of them show clusters of foreign particles (<10 µm) made up of Fe-Ni, Cr-Ni or Fe alone, typical of the abrasion of stainless steel (Powell and others 2000). Others have a complex composition, consisting of a dark phase embedded in a light one (Fig. 1).

The dark portion is $CaCO_3$ and represents particles from local crustal material derived from wind-blown soil. The EDS spectrum of the light phase indicates Ca and S, probably gypsum of secondary origin. Sulfation of $CaCO_3$ particles may take place according to the following reactions:

$$\begin{aligned}&CaCO_{3(s)} + SO_2(g) + 0.5O_2(g) + 2H_2O(v/l)\\&\quad = CaSO_4{*}2H_2O + CO_2(g)\\&\Delta G^\circ = -68.7\ \text{kcal/mol}\ (T = 298^\circ K)\end{aligned} \tag{1}$$

$$\begin{aligned}&CaCO_3(s) + H_2O(l) + H_2SO_4(l)\\&\quad = CaSO_4{*}2H_2O + CO_2(g)\\&\Delta G^\circ = -\ 19.6\ \text{kcal/mol}\ (T = 298^\circ K)\end{aligned} \tag{2}$$

Actually, the process leading to gypsum formation is not known. Pathways involving gas-phase (reaction 1) or aqueous phase (reaction 2) may occur, but the gas-phase reaction is expected to be more significant, being thermodynamically favoured even at higher temperatures. Calcium sulphate was found only in the coarsest particles, whereas $CaCO_3$ particles were ubiquitous. In addition, biological and organic materials, characterized by EDS spectra with high background values and low X-ray counts, were found in the coarse fraction.

The 20–10 µm fraction (medium-size particles) contains both irregularly or rounded shapes. Among the latter are particles consisting mainly of iron, probably iron oxides (Fig. 2), the source of which is attributed to gas-particle conversion from a high-temperature process (Aragon Piña and others 2000).

Lead-rich particles are identified among the irregularly shaped ones, some showing the Pb-Br-Cl association typical of gasoline combustion. This finding is notable as lead in this chemical form is more bioavailable than Pb hosted in the more stable minerals of the soil components. Particles containing Zn, Cu and Sb are also found, probably resulting from the abrasion of tyres and brake linings (Dietl and others 1997; Helmers 1996; Heinrichs and Brumsack 1997). Bismuth and barium are also present within this group.

Lastly, the finest particles (<10 µm) contained a series of trace elements: Pb, Sb, Sn, Fe, Zn, Ba, Cu, Bi and rare earth elements (REE) (Fig. 3). They probably derive from combustion processes, especially automotive traffic, as indicated by the presence of lead. That is also supported by their density (>2.9 g/cm^3) and ferromagnetic properties, both characteristics generally belonging to exhaust particles.

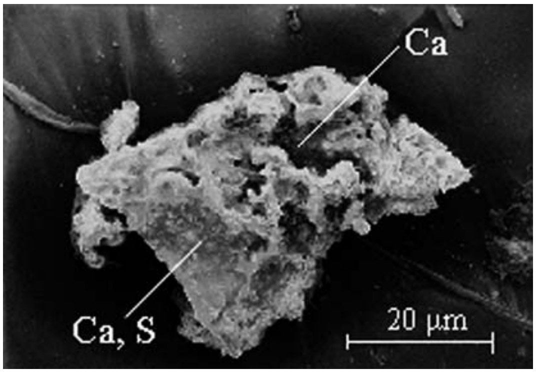

Fig. 1
Photomicrograph of a calcite particle showing gypsum of secondary origin

Bulk chemical composition of the urban road dust

A total of 37 chemical elements were determined in each subsample of urban dust (Table 1). Seven elements (Ca,

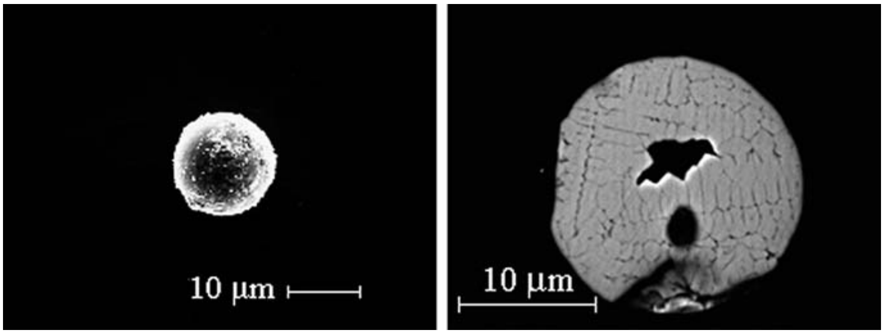

Fig. 2
Fe-rich spherical particles found in the analysed roadway dust sample

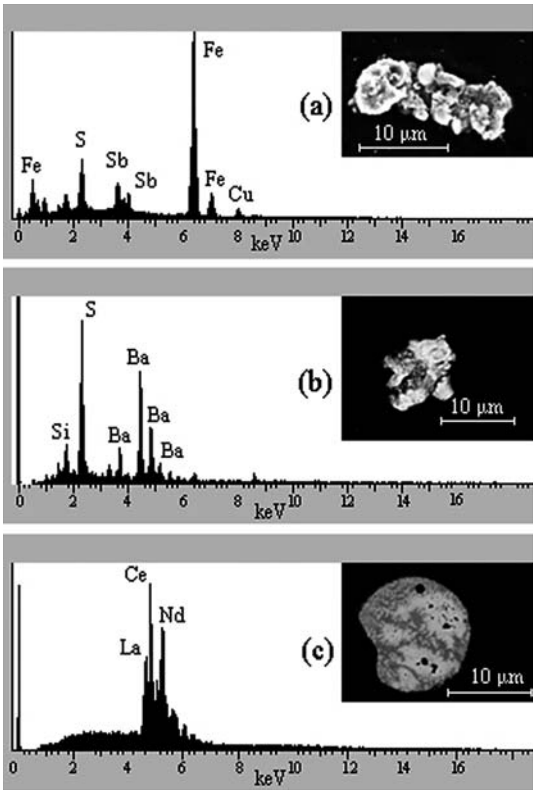

Fig. 3
SEM images and EDS spectra of particles containing Pb, Sb, Ba, Cu and Fe (**a**), Ba, Si and S (**b**), and La, Ce, Nd (**c**)

Mg, Al, Ti, Fe, K, Na) account for 99% of the total analysed inorganic burden in the 500–250 µm fraction, but fall to 97% in the finest size fraction. They are all typical crustal elements, and confirm that local rocks and soils constitute the predominant source of the collected materials. Si was not determined in this study, but is also expected to be a major component.

Figure 4 plots Ca, Al and Fe relative concentrations observed in the five dust subsamples together with those from local outcropping rocks. The representative point of “Terra Rossa”, an iron-rich soil sporadically present in some areas of the city, is also shown. Figure 4 and Table 1 reveal that calcium is the predominant element among the analysed elements, indicating that the major contribution to airborne particulate matter comes from the erosion products of nearby carbonate rocks. Helmers (1996) found an accumulation of Al in samples of common grass collected in the vicinity of a motorway with relatively high traffic and attributed increasing Al concentrations to the thin wash coat of alumina spread to the surface of catalytic converters. We also observed, by SEM/EDS analysis, traces of Al and Ca in the exhaust emissions from a car equipped with a catalytic converter. Nevertheless, in roadway dust the anthropogenic source of Al may be considered negligible with respect to the natural source. On the basis of Fig. 4, it was assumed that the main components of roadway dust come from the local substrate (LS), made up of carbonate rocks (80%), clay minerals (10%) and the “Terra Rossa” soil (10%).

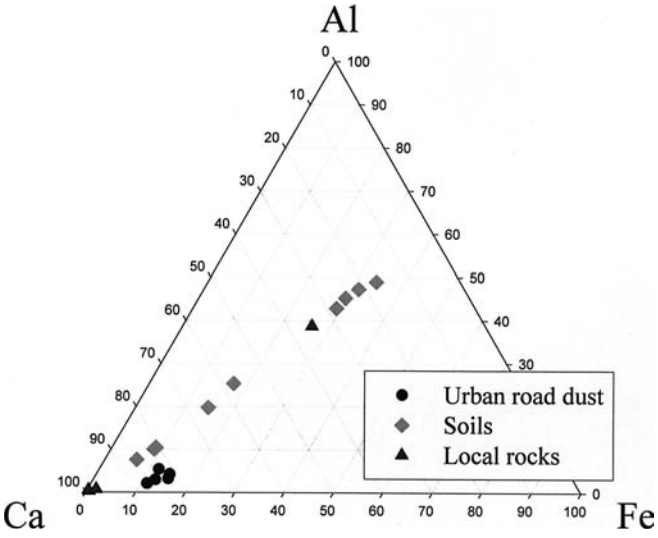

Fig. 4
Ca-Al-Fe ternary diagram relative to urban road dust, local rocks and soils

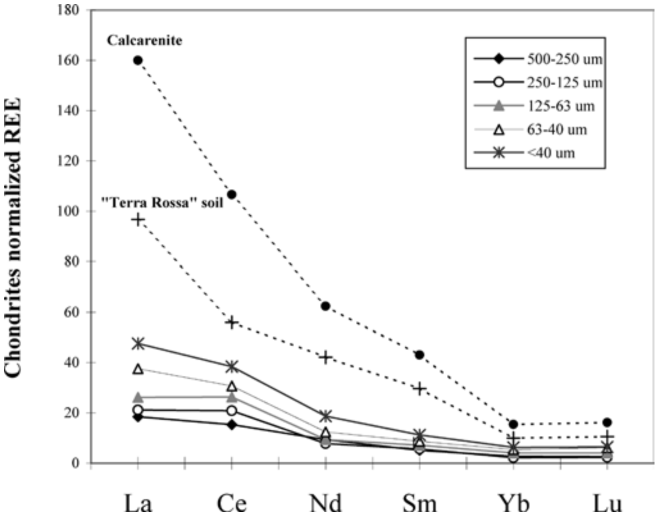

Fig. 5
REE distribution in the main lithotypes of Palermo and in roadway dust samples. Data are normalized to REE abundances in chondrites

REE are widely applied in geochemistry as tracers of rock-forming processes and to identify particular rock types. From this point of view, they may be used as markers to trace atmospheric deposition of particulate matter (Dongarrà and Varrica 1998; Chiarenzelli and others 2001). Chondrites normalized REE patterns for the five dust subsamples are shown in Fig. 5, along with those regarding two main lithotypes present in the study area. Dust and local substrates show very similar patterns, suggesting their common origin. However, a positive Ce anomaly cannot be ruled out. Ce is widely employed in automotive catalytic converters, where it is introduced as CeO_2 to promote the water–gas shift reaction and to store oxygen (Helmers 1996; Zereini and others 2001).

Enrichment factors

To identify chemical elements introduced into the environment as a result of human activities, it is common practice to calculate the enrichment factor of an element X (EFx) in the sampled material with respect to its natural abundance in the earth's crust, according to the following algorithm: $Efx=(X/E_{ref})sample/(X/E_{ref})crust$, where X is the concentration of the element of interest and E_{ref} the reference element for normalization. Generally, E_{ref} is chosen among elements of definitely natural origin (Al, Sc, Ti, etc.). According to the above equation, an element is considered geogenic when its enrichment factor is around 1, and is considered enriched when its EF exceeds 1. Nevertheless, caution must be exercised in the choice of the reference substrate, due to the great variability in trace element contents of rocks of even similar bulk composition. Reimann and De Caritat (2000) discourage the indiscriminate usage of enrichment factors indicating some shortcomings of EFs as the variable composition of local substrates compared to the average crust, the fractionation of elements during their transfer from the crust to the atmosphere and the impact of biogeochemical processes. In the present study, as the average crustal composition is rather different from the substrate of the study area (mainly limestone), to minimize possible sources of errors we decided to use the sum Σ(Ca + Mg + Al + Na + K + P + Ti) in the local substrate (LS). Enrichment factors in the various size fractions are shown in Fig. 6.

The first group of elements (Pt, Pd, Au, Pb, Br, Sb, Zn, Cu) shows very high EFs, which in some cases exceed 100. The second group has EFs in the range 0.7–3, showing that these elements are not enriched with respect to the local substrate and clearly pointing to a crustal origin, without any significant anthropogenic contribution. Some elements (Mo, Ba, Fe, Cd, P, Cr) show only minor enrichment, between the first and second groups. Although their origin is not quite clear, an anthropogenic contribution cannot be excluded.

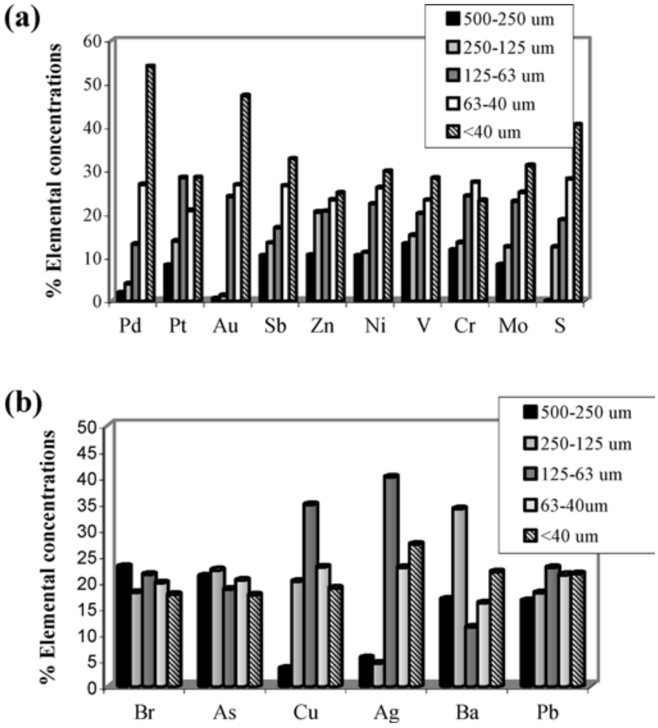

Fig. 7
Relative elemental concentrations in the five fractions of road dust. **a** Elements that build up in the finest particles; **b** elements whose concentration is independent of the selected size fractions

Figure 7 shows the relative trace element concentrations in the five mode particles. Most of them (Pd, Pt, Au, Sb, Zn, Ni, V, Cr, Mo, S) exhibit a substantial build-up in the finest particles whereas Pb, Br, As, Cu, Ag and Ba seem to be almost independent of the selected size fractions. With regard to Pb, As and Br, this may be because they form volatile compounds which adhere to pre-existing particles of any dimension. Contrary to the general trend, Cu is present in a higher percentage in the 125–63 μm size class,

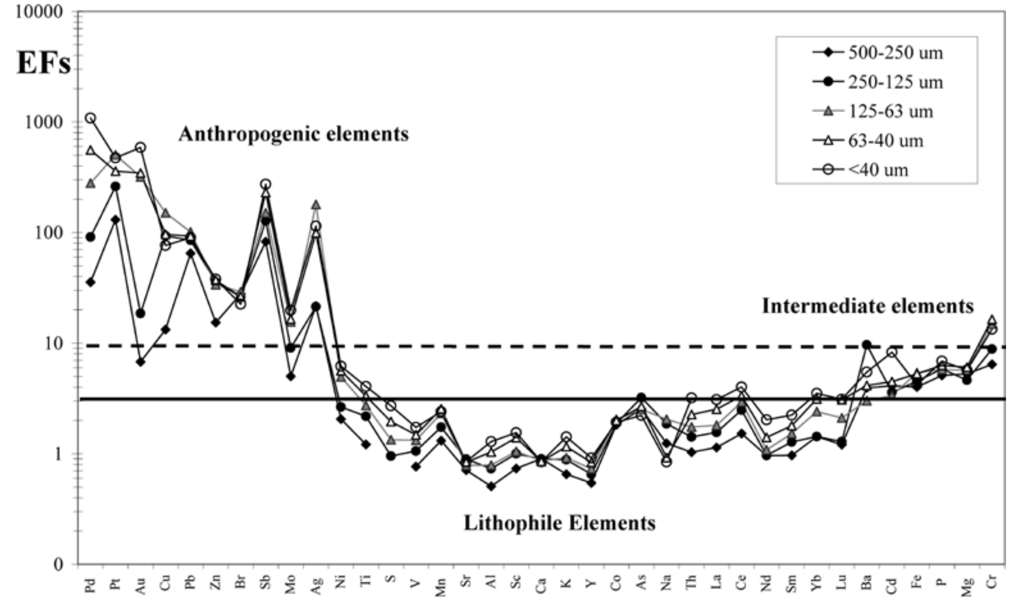

Fig. 6
Enrichment factors in the various size fractions computed using the sum Σ(Ca + Mg + Al + Na + K + P + Ti) as reference elements and average concentrations in the local substrate (*LS*)

and Ba in the 250–125 μm class. The elevated presence of some trace elements in the finest size fraction may indicate a local anthropogenic source, probably related to city traffic, as well as to long-distance transport. However, according to the element distribution maps reported by Alaimo and others 2000, metal concentrations are highest within the urban area and decrease immediately farther inland. Zn, Cu and Mo may come from several sources. Zn is mainly emitted from tires and Cu and Mo from brake-lining materials. They are also known to be used as additives to impart special qualities to oils used as lubricants, anti-oxidants and anti-corrosives (Heinrichs and Brumsack 1997; Weckwerth 2001).

Source of lead

Lead concentrations in the analysed five subfractions vary in the range 544–755 μg/g. Lead has been found in particles of high density (>2.9 g/cm^3), independently of their ferromagnetic properties. The measured isotopic ratios of lead have to be compared with the signatures of potential sources. During 1997–1999, the ^{206}Pb/^{207}Pb ratios in alkyl lead gasoline sold in Sicily by the major companies were in the range 1.066–1.137 (average: 1.104; Monna and others 1999; Aiuppa and others 2001). These signatures indicate a significant utilization of remote and non radiogenic lead ore deposits (probably Canada and Australia). On the other hand, uncontaminated local sedimentary substrates exhibit comparatively more radiogenic values, with ^{206}Pb/^{207}Pb ratios ranging from 1.169 to 1.200. Dust from urban incinerator of Palermo and Messina, taken as representative of industrial emissions, yielded intermediate ^{206}Pb/^{207}Pb ratios, between 1.14–1.16. On the basis of enrichment factor (EF_{Pb} ~100), it is clear that the present road dust samples contain solely a small fraction of crust-derived lead. With the exception of the 500–250 μm non magnetic subsample, which reflects a greater influence of crustal-derived lead, there is no significant difference among and within the five samples, showing ^{206}Pb/^{207}Pb ratios in the range 1.137–1.149 (Table 2). Such values are not typical of the gasoline signatures reported above, nor airborne particulate matter collected at Palermo during 1997–1998 (^{206}Pb/^{207}Pb ~1.106–1.123; Aiuppa and others 2001). High ^{206}Pb/^{207}Pb ratios (1.156) have recently been reported in gasoline samples from Milan, Italy, and such a value is consistent with airborne particulate matter collected at Venice during the same period (^{206}Pb/^{207}Pb ~1.148–1.151) (Bollhöfer and Rosman 2001). Thus, it seems that because of the recent phasing out of lead from gasoline, this polluting source has considerably decreased at Palermo, while the contribution from local industrial activities is now better distinguishable in road dust.

Antimony

Antimony was predominantly found in the finest particle size (<40 μm) at a concentration of 50.8 μg/g, about threefold that found in the 500–250 μm class, and a hundred times higher than its average concentration in crustal material. Several studies have focused on the anthropogenic sources of antimony in atmospheric particles. According to Ondov and others (1982), gas exhausts from gasoline combustion account for about 20% of atmospheric Sb. Pacyna and others (1984) reported that the other main sources of Sb are combustion fumes from petrol products, thermoelectric plants and refuse incinerators. Antimony is also employed in alloys for motor bearing, due to its stabilizing properties (Fowler and Goering 1985), and its presence in airborne samples from urban areas has been found to be closely associated with traffic (Peichl and others 1994), due to abrasion of tires and asbestos-free brake linings. Dietl and others (1997) used X-ray spectroscopy to measure antimony concentrations in brake linings, finding a range of 1–4 %. Heinrichs and Brumsack (1997) and Weckwerth (2001) found enrichment factors for Sb in brake-lining components between $2{\cdot}10^4$ and 10^5, which are higher than in any other known material. In our study area, an increase in antimony concentration in pine needles with decreasing distance from zones of higher traffic density was found by Alaimo and others (2000). A strong correlation between antimony and lead was also described by Aiuppa and others (2001). All these findings support the recent proposal of Cal-Prieto and others (2001) to use the Sb content as a tracer of anthropogenic influence in environmental studies. Sb toxicity is high and may have permanent effects in even limited ingestion doses in humans.

PGE and gold

Pt and Pd concentrations in the five fractions vary in the range 115–396 and 37–1070 ng/g, respectively. Pd in the <40 μm particle size is two orders of magnitude higher than in the 500–250 μm class, while Pt is three times higher. The observed concentrations are by far greater than those in the earth's crust and in some soils of Palermo (range 0–2 ng/g for both Pt and Pd). An interesting trend is seen in Fig. 7, in which the relative concentrations of both elements increase with the decreasing of dust size category. These results are consistent with those found in Germany (Schäfer and others 1999; Zereini and Urban 1994) and in the UK (Hutchinson and others 2000). Data demonstrate that vehicle emissions constitute also an important source of Pt and Pd in the environment, these elements being mainly concentrated within the urban area. Although Pt and Pd deposition due to emissions from catalytic converters is still limited, it does have a significant impact on the urban environment, as the natural background values are quite low.

Gold concentrations were found to lie in the 72–5,930 ng/g range, the highest value occurring in the <40 μm fraction. Although gold is not employed in the catalysts industry because of its high catalytic reaction temperature, such elevated concentrations are not unexpected. It has been found in microsize particles emitted by cars equipped with catalytic converters, and concentrations in excess of 437 ng/g were found in airborne dust from Germany (Zereini and others 2001). Further confirmation of the anthropic origin of gold in airborne particulate matter comes from the findings of Dongarrà and others (2002), who observed the anomalous presence of gold in the city air of Palermo with respect to the outskirts.

Conclusion

The obtained results indicate that the common practice of monitoring total solid particles (TSP), as generally done by the municipal agencies for the environment, cannot be considered exhaustive in a modern approach to environmental control, being inadequate to evaluate the impact of anthropogenic activities in urban areas and, therefore, not satisfying from a sanitary point of view. This study may be of value for follow-up studies aimed at assessing municipal and industrial pollution and suggests some recommendations.

1. For effective strategies in pollution control, more attention must be paid to distribution of trace elements in airborne particulate.
2. The frequent association of some elements in airborne particles, together with particle morphology, may assist in identifying their mode of production and the relative significance of various emission sources.
3. Any attempt to assess the effects of TSP must rely both on measurements of elemental composition as a function of particle size and on the chemical and physical forms of metals in air.
4. There is a need for interdisciplinary studies of the emission rates of heavy metals in the urban environment and assessment of their deposition on topsoils, vegetation and hydrological systems, in order to provide reliable data for receptor models and dose- response analyses.

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