

# PLATINUM AND HEAVY METAL CONCENTRATION LEVELS IN URBAN SOILS OF NAPLES (ITALY)

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## SUMMARY

Cd, Cu, Hg, Pb, Zn and Pt concentrations were determined in soil samples collected in the urban area of Naples (Italy). Particular attention has been posed on Pb and Pt content, due to their presence in vehicle emissions.

The results evidence that Pb (mean 71, range 19 - 318 mg/kg) and Pt (mean 8.5, range <1-13.8 ng/g) concentrations are comparable with those found in other Italian urban soils. The concentrations of Zn, Cu, Cd and Hg are generally close to those of unpolluted soils. Higher heavy metal concentrations have been found in top soils and, in particular, the relatively high concentration levels of Pb suggest that the main pollution source could be related to vehicular emission.

Zn, Cu, Pb, Cd and Hg are enriched in finer soil fraction, while Pt content does not show any relation with soil particle size.

Data concerning Pt represent the first attempt to measure this element in urban soils of Naples and can be used as a reference level to evaluate a possible long-term accumulation trend following the introduction of the automobile catalytic converters.

**KEYWORDS:** Automobile catalytic converters, heavy metals, ICP-MS, platinum, urban soils.

## INTRODUCTION

Heavy metals content in urban soil is mainly associated to anthropogenic activities and, in particular, Pb and Pt can be related to vehicle emissions. During the last decade, paralleling the introduction of unleaded fuel, an evident decrease of Pb levels in air and, consequently, as a long term effect, in soil has been observed; while, after the introduction of automobile catalytic converters, a general increasing trend, even if still moderate, for Pt and other

related Platinum Group Elements (PGEs) has been detected [1-4]. These elements, strictly related to the airborne particulate matter, could have a relatively high mobility, that is higher with respect to "pedogenetic" elements, producing some concern over the possibility of their dispersion in urban environments and resulting in a possible human health hazard [5-7].

Studies on trace elements distribution in Italian urban soils are relatively scarce [8, 9] and mainly devoted to Pb and some other heavy metals, while studies on PGEs, in most cases, deal with airborne particulate matter and road dusts [4].

The city of Naples is affected by a wide variety of anthropogenic activities and pollution can be mainly related, at present, to vehicular traffic emissions, housing and manufacturing industries, while, until 80's, metal processing industry, located in the northeastern part of the city, has also been relevant [10].

This work aims at studying the distribution of selected heavy metals (Cd, Cu, Hg, Pb, Zn and Pt) in urban soils of Naples and the relation between trace element content and soil grain size fractions. Moreover, a comparison of the present situation in Naples with those of urban soils of other Italian cities has been done.

## MATERIAL AND METHODS

Ten soil samples were collected from five sampling sites (characteristics are reported in Table 1) in the Metropolitan area of Naples. In each area both samples from dumped material and relatively undisturbed soils have been collected. Two levels were sampled at the depth of 0-10 cm (top, T) and 40-60 cm (bottom, B), respectively, from the relatively undisturbed soils, and, in addition, top soil samples were collected from dumped materials (D), chosen among those closest to main roads, for a total of 15 analytical samples.

TABLE 1 - Characteristics of the sampling sites.

Sampling sites	Characteristics	Traffic intensity
1	East side of the city. Mainly residential area (Quartiere Ponticelli), about 4 Km from industrial refinery area (S.Giovanni a Teduccio)	Medium- high
2	Central green area (Villa Floridiana, about 30 ha). The dumped soil was sampled just outside of the park	High in the surrounding area
3	Central area of Fuorigrotta. Samples 3T and 3B were collected in an area far from main traffic lane. Sample 3D was collected close to a tunnel with very high traffic intensity.	High
4	Bosco di Capodimonte (30 km <sup>2</sup> ). Sample 4D was sampled just outside of the green area and close to the motorway ring.	Very high
5	Northern part of the city, Camaldoli area. Green and residential area (Bosco Cinque Querce).	Low

Soils samples were dried at 40 °C and sieved through a 2 mm sieve. Then the following size fractions were obtained: 2-0.5 mm; 0.5-0.063 mm; <0.063 mm. The total <2 mm sample and each sieved fraction were weighed and the weight percents of the fraction calculated. After homogenisation, each sample was ground in an agate ball mill, obtaining a fine homogeneous powder, and metals extraction was carried out on the total and on the size-fractionated samples by means of 'aqua regia' (10 ml), in a microwave oven.

Analyses of Cd, Cu, Pb, Pt and Zn, were performed by ICP-MS (Perkin Elmer, Elan 6100). Hg was determined with a Direct Mercury Analyzer-80 (DMA-80, Milestone Inc., Monroe CT).

Materials and reagent blanks were prepared following the same procedure.

Certified reference materials (CRMs) for Pt in soils and in concentrations similar to those expected are not available. We have analysed the road dust sample CW7 (from PACEPAC project), obtaining a Pt concentration of  $55.10 \pm 1.60$  ng/g, very close to  $55 \pm 8$  ng/g given by Gomez et al. [11].

The analytical procedure for the other elements was previously tested using CRMs (Table 2). Analyses were performed at ENEA-TEIN-CHIM Labs (Rome).

TABLE 2 - Results of certified reference material (BCR 141 R, soil), values in mg/kg.

	Certified values	Found values
<b>Pb</b>	$51.3 \pm 2.0$	$54.9 \pm 0.7$
<b>Cu</b>	$46.9 \pm 1.8$	$44.3 \pm 1.0$
<b>Zn</b>	$270 \pm 8$	$264.1 \pm 1.6$
<b>Cd</b>	$14.0 \pm 0.4$	$14.8 \pm 0.2$
<b>Hg</b>	$0.24 \pm 0.03$	$0.24 \pm 0.01$

## RESULTS AND DISCUSSION

The concentration levels of the elements analysed in the selected urban soil samples of Naples (Table 3) are generally low and comparable with those considered for Italian urban soils (Table 4). The highest heavy metal contents have been found in dumped soils; these samples also show a wide concentration range that confirms their heterogeneous composition. In relatively undisturbed urban soils, trace elements concentration decreases with depth, showing values very close to those considered as typical for Italian natural soils [12] (see Table 4, last line).

Pb concentration (mean value 71, range 19-318 mg/kg) exceeds Italian natural soils background levels (NSBL), while it is lower with respect to the values of other Italian cities.

Cu concentration (mean value 63, range 8-160 mg/kg), is higher than Italian NSBL, while it is comparable, on average, with other Italian urban soils (Table 4).

Zn shows a concentration (mean value 63 mg/kg) close to that of Italian NSBL, even if some samples show higher concentrations (range 41-226 mg/kg) typical of polluted soils and comparable with those found in other urban areas.

Instead, Cd (mean value 0.3, range 0.1-0.8 mg/kg) and Hg (mean value 0.12, range <0.01-0.43 mg/kg) concentrations in both dumped and relatively undisturbed Naples soils were very similar and, in some cases, lower than the values considered as typical for Italian NSBL.

The concentration of Pt (mean value 8.5, range <1-13.8 ng/g) is slightly higher with respect to the geochemical background for soils developed on various bedrock types (range 2-5 ng/g) [1, 13]. Pt can be mainly related to the emission of automobile catalytic converters, and the existence of slight early contamination phenomena, related

**TABLE 3**  
Mean and standard deviation of the studied metals in Naples urban soils (total <2 mm samples).

	Zn (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Hg (mg/kg)	Pt (ng/g)
“Undisturbed” Soils						
(0-10 cm)	83±13	62±42	62±21	0.3±0.1	0.16±0.15	8.1±2.3
(40-60 cm)	66±16	47±50	42±15	0.2±0.1	0.08±0.06	7.7±2.1
Dumped Soils (0-10 cm)	105±69	81±61	109±119	0.4±0.3	0.11±0.13	10.0±2.9
All samples	84± 42	63±50	71±71	0.3±0.2	0.12±0.12	8.5±2.5

**TABLE 4**  
Heavy metal concentrations in urban soils of some Italian cities and Italian natural soil background concentration levels (a).

	Samples	Zn (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Hg (mg/kg)	Pt (mg/kg)	Ref.
Naples	15	84±42	63±50	56±22	0.3±0.2	0.12±0.12	8.5±2.5	
Rome	48			330±252	0.31±0.29		11.5±4.7	1
Florence	26	138±35	71±29	103±41				9
Palermo	37	143±52	74±35	256±79			3.60±0.90	(b)
Italian natural soils (a)		40÷110	20÷70	10÷60	0.1÷1.5	≤0.1÷1	≤2÷5	12

(b) Unpublished data (obtained in our laboratories).

to the introduction of these devices, can be evidenced. In fact, in the samples studied Pt concentrations are higher in dumped soils (mean value 10, max 13.8 ng/g), collected close to main traffic roads. Moreover, topsoils are enriched in Pt with respect to bottom soils (Table 3), thus confirming the possible recent deposition of atmospheric particulate matter, containing vehicle emitted Pt particles.

**TABLE 5 - Weight percents of the considered grain size fractions (mean and standard deviation).**

Size fraction	Weight %
> 2 mm	15.6±7.7
2÷0.5 mm	19.4±4.8
0,5÷0.063 mm	45.0±6.2
<0.063 mm	20.0±6.2

Granulometry is an important factor for the abundance of trace elements in soils and sediments, in fact, their concentration is highly correlated with the grain-size distribution [14, 15]. The soils analysed show a homogeneous grain-size distribution pattern. They are preferentially sandy soils, being the 2÷0.063 mm fraction about 65% of the total sample (Table 5).

The content of Cd, Cu, Pb, Zn and Hg in the majority of analysed samples increases with decreasing grain size, showing a relative enrichment in the fraction <0.063mm. As an example we have reported the behavior of Pb in samples from sites 3 and 4 (Fig. 1). This is generally attributed to the higher content of organic matter in finer fractions and to the fact that the trace metals tend to concentrate both within clay minerals lattice and on the surface of soil particles, hence, the finer fractions have larger specific surface areas, which leads to the increase of metal sorption intensity [14, 16].

A similar pattern has been observed for all elements considered with the exception of Pt. No relation, in fact, has been observed between Pt and soil grain size fractions.

First, this fact can be due to the very low concentrations of Pt in urban soils, leading, at the present time, to a difficult discrimination between the natural content (background levels) and the contribution due to the deposition of vehicle-emitted Pt particles. These aspects were examined by Wei and Morrison [17]. They, however, at least for road dusts and kerbside sediments, observed a slight increase in the <0.063 mm fraction and related this occurrence to the fact that the median size of Pt particles emitted from catalysts is 5-10 µm [18].

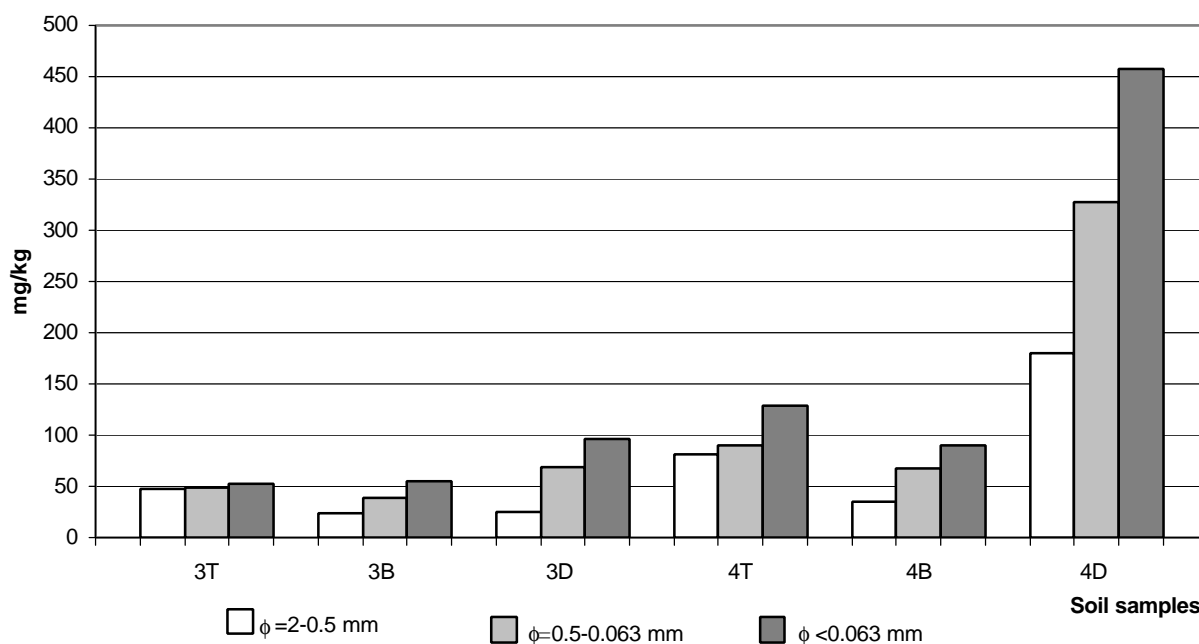


FIGURE 1

Pb distribution in grain size fractions of soil samples collected from high traffic intensity areas (T=top, B=bottom, D=dumped).

Even if a slight increase in Pt concentration levels can be already noticed, at present, this trend is obviously more evident in airborne particulate matter and road dust than in urban soils (and other environmental matrices, as river sediments). Moreover, lead and platinum associated to particulate matter are generally not readily mobilized and redistributed in the various grain size fractions of soils.

## CONCLUSION

The analysis of data concerning concentration levels of the studied elements in the selected urban soils samples of Naples show that Pb and Pt are comparable with those found in other Italian urban soils, while the concentrations of Cd and Hg (and to a lesser extent of Zn and Cu) are close to those of unpolluted soils.

In particular, the concentration range of Pt (<1 - 13.8 ng/g) is relatively higher with respect to the values considered as the geochemical background (2-5 ng/kg). This fact evidences the possible existence of early contamination phenomena related to the introduction of catalytic converters.

Higher heavy metal concentrations have been found in top soils, while the highest concentration characterize dumped soils, owing to their closeness to main traffic roads.

Grain-size distribution considerably affects trace elements content in these urban soils, with the exception of Pt. In fact, while Zn, Cu, Pb, Cd and Hg concentrations increase with decreasing grain size, Pt content does not show any relation with soil particle size fractions.

This can be due to the very low concentrations of Pt in urban soils, leading to a difficult discrimination between the natural content (background levels) and the contribution due to the deposition of vehicle-emitted Pt particles.

Even if a slight increase in Pt concentration levels can be already noticed, at present, this trend is obviously more evident in airborne particulate matter and road dust than in urban soils.

This work can be considered as a preliminary study on heavy metal distribution in Naples urban soils and further work is necessary to evaluate the general validity of conclusions. In fact, on the basis of this experience, new sampling areas will be investigated taking into account traffic intensity, soil morphology and prevalent wind direction.

Since the number of cars equipped with catalytic converters is increasing in Italy, the Pt concentration should be monitored over the next years.

The presence of potentially harmful elements, such as Pt, in the fractions containing inhalable particles, could be, in fact, considered as a potential risk for the population.



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