Contribution of a municipal solid waste incinerator to the trace metals in the surrounding soil

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Abstract This study analyses the pedological environment of the area near a municipal waste incinerator that has been operating in the southeast district of Pisa for approximately 20 years. There are many other industrial activities in the area besides the incinerator, which represent possible sources of pollution, as well as heavy road traffic. The study area was defined by a 0-4-km zone around the site with a population of approximately 12,000 residents. The study included the physical and chemical characterisation of 100 samples of soil and an analysis of trace metals such as Cr, Ni, Pb, Zn, Hg, As and Cd. The samples were grouped into soil use categories. The results showed Zn, Pb and Hg correlated with their potentially mobile fractions, and suggested an anthropic contribution to their presence in the soil. Ni, Cr and As showed values attributable to a lithological origin. This was consistent with the PCA results. The aim was to define the environ-

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NMR Centre, Department of Chemistry, University of Siena, Viale Bracci, c/o Policlinico "S.Maria alle Scotte" 53100 Siena, Italy mental state of the soil of the area in order to create a reference for future research and to verify the possible presence of pollution from other sources (local industrial activities and traffic).

Keywords Lead · Zinc · Principal component analysis · Sequential extraction · Urban · MSWI

Introduction

Using a municipal solid waste incinerator (MSWI) is a common option for managing waste, especially for areas lacking in landfill capacity. However, the toxicity of the emissions can cause great concern for the population living nearby. Trace metals such as lead, copper, nickel, cadmium, arsenic, mercury, chromium and zinc are some of the contaminants present in the emissions, some of which can contaminate the surrounding environment. An increase in manganese and zinc (Rovira et al. 2010), lead (Collett et al. 1998), lead and mercury (Cangialosi et al. 2008) and cadmium (Morselli et al. 2002) has been found in the surface soils near MSWIs.

As very often, these kinds of plants are situated in populated areas, near the influence of anthropic activity, other sources can mask the impact of the MSWI (Llobet et al. 2002; Rimmer et al. 2006). Nadal et al. (2005) stated that the influence of a hazardous waste incinerator on the increase in metals in soils is minimal in relation to other metal pollution sources along an urban–rural gradient. Knowledge of the main use of the soil in a particular area may be of help in order to interpret the results of an environmental survey, as it can reveal different practices (tillage, fertilisation, chemical treatments) or inputs (vicinity to traffic, presence of waste material) or side effects (compaction), which may lead to differences in the fate of pollutants. Moreover, knowing how the soil is used may help in assessing human health hazards and risks (Boyd et al. 1999).

It is very important in this type of study to know soil parameters, such as pH, organic matter (OM), texture and cation exchange capacity (CEC). These parameters can influence the behaviour of metals in soil, seeing as soil is a dynamic system and is subject to short-term fluctuations in conditions. pH influences the behaviour of metals: in general Pb, Zn, Ni, Hg and Cd are more mobile under acidic conditions, whereas the opposite is the case with Cr and As (Beesley et al. 2010). The solution/adsorption equilibrium of trace metals can be influenced by the presence and the status of OM, and the percentage and quality of the fine mineral fraction. If the OM is stable, then complexes of high stability can be formed between metals along with humic substances, and thus the mobility of metals is reduced. In different conditions, the presence of OM can improve the soluble fraction of trace metals (Alloway and Jackson 1991; Bermudez et al. 2010). Fine mineral fractions (silt and clay) can absorb pollutants on its surface and reduce the concentration of metals in the soil solution and thus its bioavailability (Brazauskiene et al. 2008).

It is important to investigate the potential mobility of metals in order to quantify any possible threat to the population, since these fractions are the most available. Metals can penetrate the cell membrane of roots and end up in the food chain.

Multivariate analyses are used for environmental studies and give an objective and scientific consistency to the collected data, since they bring together all the information from interactions and patterns hidden in the dataset (Manta et al. 2002; Li et al. 2004; Zhang 2006). In this study, principal component analysis (PCA) was used to highlight the differences and the similarities in the origin and distribution of the metals.

There were two main aims of the study, firstly, to evaluate the presence of trace metals in the soil around a 20-year-old MSWI plant, and secondly, to evaluate the mobility of the metals and assess their relation with the soil's properties, such as texture, organic matter and pH and also soil usage. The final target was to make a hypothesis on the contribution of the MSWI and the interactions of other possible sources of pollution. The study is part of a project funded by local authorities to plan the construction of a new hazardous waste treatment plant.

Materials and methods

Location of the research and sampling

The MSWI is located in the peri-urban area of Pisa, Italy (Fig. 1). There are approximately 120,000 inhabitants in the area (the municipality of Pisa plus the smaller towns nearby). The annual mean air temperature is 14.3°C and the annual mean rainfall is 900 mm. Figure 2 shows the map of the MSWI area. The area surrounding the MSWI is located within a network of very busy roads that lead to the city, and includes agricultural activities and light industries. In order to provide a sampling map, the incinerator was taken as the centre of the area. To monitor the area of influence of the MSWI the surface was divided into five concentric circles, with radii of 400, 800, 1,400, 2,700, and 4,000 m. A grid with a regular square mesh of 500 m was created, on the basis of this the sampling points were chosen as close as possible to the map point originally individuate with a GPS, where the open soil was reachable, with "judgmental criteria" as in Rimmer et al. (2006). Two more sampling areas were chosen as a control in the nearby countryside, where the influence of the incinerator was considered irrelevant respectively at 4,500 and 5,800 m, Fig. 2 shows their location out of the circles of influence of the MSWI. One hundred samples were collected all at the same depth (0-20 cm), and each sample consisted of three sub-samples obtained in a quadrate of 1×1 m, the surface layer was







Fig. 2 Map of the Pisa area showing the sampling points, the buildings and the MSWI (Maio et al. 2006). The *circles* represent the area of influence of the incinerator, the sampling points out of the circles are the controls

not eliminated as reported in Theocharopoulos et al. (2001); the sampling distance from the roads was always >2 m. Each sampling point was georeferenced using a GPS device, and a brief description was added (see map in Fig. 2). The criteria used in the description were the main usage (e.g. cultivated or not) and the vicinity to possible sources of pollution (e.g. roads, parking areas, canals). The description included a more detailed identification of the site and in addition, located each sampling point in its real context, thus helping us to interpret the results of the analysis. On the basis of the description, the samples were grouped into three categories: agricultural (AS), urban (US) and natural (NS) with reference to cultivated soils, i.e. tilled and possibly treated with chemicals (fertilisers, herbicides). The main crops of the area were wheat, sunflower and generally field crops. US referred to soils disturbed by the action of a strong anthropic context, including urban, residential and roadsides. NS referred to undisturbed soils such as those clearly abandoned, uncultivated or wild.

Soil analysis

The samples were taken at a depth of 0-20 cm. Soil was air-dried at room temperature, sieved in a 2-mm mesh and analysed for pH, organic matter, CEC and texture. Texture was determined using the pipette method (Gee and Bauder 1986). CEC was determined using an ammonium acetate method, pH in water and OM with the Walkley-Black method, and all the methods were described in Methods of Soil Analysis of the ASA-SSSA (1996). The concentrations of Pb, Cu, Ni, Cd, As, Hg, Cr and Zn were measured after nitricperchloric microwave digestion by atomic absorption spectroscopy (AAS), equipped with graphite furnace for As analysis and equipped with hydride generation for Hg analysis (Wright and Stuczynski 1996). The AAS detection limits for the elements were as follows: As 0.06, Cd 0.001, Cr 0.004, Cu 0.002, Hg 0.15, Ni 0.005, Pb 0.01 and Zn 0.0006 mg l⁻¹. Soil samples also underwent a sequential chemical extraction with H2O, KNO3 and diethylene triamine pentaacetic acid (DTPA) in order to investigate the chemical forms of some of the metals (i.e. lead, nickel, copper and zinc). This sequential extraction procedure evaluates the potential mobility of metals: the H₂O extractable is the mobile fraction, and the KNO₃ extractable is the fraction weakly bound to the solid phase with electrostatic bounds. The DTPA fraction is strongly bounded to the solid phase with a covalent link. DTPA extractant was prepared according to Lindsay and Norvell (1978). Details of the sequential extraction are described by Petruzzelli (1989) and were used to evaluate metal mobility in accordance with Barbafieri et al. (1996). For each metal quality assurance and quality control were performed by testing standard solution every ten samples. Certified reference material (CRM 024-050) was used to control the quality of analytical system. The recovery of spiked samples ranged from 94% to 101%.

Statistical analysis

In this study, both univariate (ANOVA with LSD post-hoc test and Pearson's correlation test) and multivariate techniques (PCA) were applied to the dataset. One-factor ANOVA was used to check for OM differences between different types of soils and pollution differences due to wind direction. The correlation test was used to evaluate the relation between metals found in soil and in the corresponding DTPA extracts. PCA was used to describe the characteristics of the soils as a means of classifying the relationships between measured variables and objects. Notable examples of PCA use in environmental chemistry are found in the work of Carlosena et al. (1998), Carlon et al. (2001), Critto et al. (2003) and Backstrom et al. (2004).

As reported by Einax et al. (1997), PCA is an unsupervised method which enables various underlying components to be spotted, which are responsible for the covariation of the observed variables. PCA linearly transforms an original set of variables into a set of uncorrelated new variables (components), which represents all the variance (information) of the original dataset. In order to choose the appropriate number of components, we used the Scree Test Criterion (Cattell 1966), which retains the factors placed before the change in slope. For each sample, it is possible to compute a score that depends on the components calculated. We used such scores for spatial analyses, in order to find out the pollution gradient over the observed area. The normal distribution of each variable was pre-checked (Kolmogorov-Smirnov test), since PCA is sensitive to outliers (Reimann and Filzmoser 2000). Non-normality was reduced using a Box-Cox transformation. Since the analytical values varied greatly among the examined parameters, transformed data were auto-scaled (zero mean and unit variance) before running the statistical analysis. The PC loadings were rotated in order to get the maximum variance, using Varimax rotation with a Kaiser normalisation.

The multivariate statistical analysis was performed using Statistica 7 (Statsoft).

Results and discussion

Soil characterisation and metal content

The statistics of the soil parameters (texture, pH, OM and CEC) and total and extractable metal contents are described in Table 1. Results for the soil characterisation revealed a high variability in the parameters, except for pH. The value of pH in all the samples was constant around 8, which is the average pH in soils of the study area and of most Italian soils, and it reveals low metal mobility. In addition, in urban areas, soils often have an alkaline pH (Bridges 1991). The percentages of sand, silt and clay were very variable (4.3-86.6%, 7.2-47.6% and 6.2-60.5%, respectively). Likewise, OM (0.45-12.4%) and CEC $(4.9-37.4 \text{ cmol } \text{kg}^{-1})$ were also highly variable, in fact the values of CEC followed the content of clay and OM.

CEC is correlated to the soil content of clay and humus, and in agricultural soils in Italy it ranges from 8 to 50 cmol kg⁻¹ (Sillanpää and Jansson 1992). In this study, the lowest value of the CEC (4.9) was probably due to the low percentage of clay in the related sample. The texture variability was high in all the categories of soil use, though in AS it was the most notably different. This was connected to the higher number of samples in this category (59), while there were 24 in the USA and 17 in NS. The heterogeneity of the vast area

of dry m	atter)			1										I				
	Cd	Cr	Ni ext	Ni tot	Cu ext	Cu tot	Pb ext	Pb tot	Zn ext	Zn tot	Hg	As	MO	CEC	μd	Clay	Silt	Sand
													(%)	(cmol kg^{-1})	(H_2O)	(%)	(%)	(%)
Mean	0.46	84.7	1.47	73.4	12.1	68.7	8.63	39.3	9.70	127	0.17	5.89	3.34	20.9	8.0	25	28	47
Median	0.44	83.1	1.35	69.5	7.90	56.9	3.94	27.9	6.50	96.9	0.15	5.60	2.64	20.8	8.0	21	29	48
SD	0.32	24.3	0.52	24.4	9.45	43.3	11.3	34.8	16.7	135	0.11	1.85	2.20	6.03	0.35	12	6	19
Var	0.10	592	0.27	597	89.2	1877	128	1216	279	18252	0.01	3.43	4.84	36.3	0.12	150	78	353
Cv	68.8	28.74	35.62	33.30	77.89	63.05	131.28	88.58	172.57	106.30	66.54	31.49	65.84	28.84	4.36	50%	31%	40%
Min	0.02	14.9	0.70	11.4	0.02	0.15	1.80	14.6	2.15	48.4	0.03	2.60	0.45	4.90	6.80	9	7	4
Max	1.30	135	3.00	121	50.1	271	76.0	207	164	1286	0.60	12.6	12.4	37.4	8.90	61	48	87
Range	1.28	120	2.30	109	50.0	270	74.2	192	162	1238	0.57	10.0	11.9	32.5	2.10	54	41	82

Mean Median SD Var CV CV Min Max

[able 1 Main physical and chemical properties and total and DTPA extractable metal content of the soils (values of metals are expressed in milligrams per kilogram



Fig. 3 Log-transformed OM values in the three categories of soils. Soils employed for agricultural purposes were the poorest and the most uniform in terms of OM content

covered by the study may be responsible for the heterogeneity of the texture.

The value of OM in the AS samples was significantly lower than the values of the urban and natural soils (p = 0.0001, LSD post-hoc test), as shown in Fig. 3. In order to check for inequalities, a one-way ANOVA test was used. To achieve a better normal distribution, the data were logtransformed and checked for outliers. The low values of OM in the AS samples confirmed that the proposed interpretation of the soil usage was correct. In fact, in soils that are regularly cultivated, the organic matter is quickly degraded. In natural soils the residues fall and are transformed into humus, which improves the OM content. In urban soils the OM content is normally very heterogeneous, due to different management practices, and soils rich in OM are found in parks or in unmanaged areas (Bretzel and Calderisi 2006).

The results of the total content of metals showed that all the values were within the limits of the Italian guidelines for contaminated sites for commercial and industrial areas (Table 2). Seven samples of soil exceeded the limits for residential areas in the case of total Cu, six samples for Pb and eight samples for Zn. Zinc reached an exceptionally high value of 1,286 mg kg⁻¹, in one sampling point and thus this outlier value was excluded from the statistics. The high value of this Zn sample may be explained by some waste that had been deposited in that exact location. The extractable values in DTPA are shown in Table 1: these values were very low in the case of Ni, while they corresponded approximately to 30% of the total value for Pb, Cu and Zn.

A strong linear correlation was found between total and corresponding extractable metals: Ni (r = 0.7325, p = 0.0001), Cu (r = 0.8341, p =0.001), Pb (r = 0.9296, p = 0.001) and Zn (r =0.9477, p = 0.01). Interestingly, unlike the other metals, the average concentration of nickel found with the DTPA extraction was nearly 100 times smaller than the average total concentration in soil. In fact, Ni and Cr are some of the "lithogenic metals" (i.e. coming to the soil directly from the parental material) typical of soils rich in serpentine minerals (ophiolites) as many Italian soils. Other studies carried out on this same type of soil found the same correlation (Biasioli et al. 2005). On the other hand, "exogenous metals are more weakly bound to the soil matrix and therefore more easily released" as reported in Abollino et al. (2002).

Multivariate analysis

Metals, total and extractable

Metal variables were also studied using PCA in order to clearly depict the correlations between

 Table 2
 Guidelines for total value of metal levels in Italian soils (values are expressed in milligrams per kilogram of dry matter)

Ref.	Cd	Cr	Ni	Cu	Pb	Zn	Hg	As
§	2	150	120	120	100	150	1	20
#	15	800	500	600	1,000	1,500	5	50

§D.M. 152/06 urban residential areas, # D.M. 152/06 commercial and industrial areas

Table 3 Principal		PC 1	PC 2	PC 3	PC 4
component loadings of	Cd	0.380969	0.04126	0.09868	0.817569
extractable metal content	Cr	-0.19052	0.760689	-0.164191	0.123176
(main correlation are	Ni_ext	0.065823	0.861424	-0.0335	0.110453
reported in bold)	Ni_tot	-0.156754	0.798944	-0.013853	0.032011
* /	Cu_ext	0.159673	-0.125691	0.926276	0.113579
	Cu_tot	0.184741	-0.038999	0.943682	-0.026997
	Pb_ext	0.853334	-0.184166	0.210434	-0.074343
	Pb_tot	0.875422	-0.244676	0.177511	-0.183733
	Zn_ext	0.843824	0.010074	0.057943	0.123338
	Zn_tot	0.873783	0.261894	0.121331	0.128016
	Hg	0.477352	-0.071549	0.004664	-0.747704
	As	0.144501	0.826376	-0.020996	-0.125794
	Exp.Var. tot	29.07%	23.57%	15.67%	11.30%

them. Four components, which corresponded to 79.62% of the total variance, have been extracted, in order to sum up and explain the most part of the original information. The original variables were grouped together, as reported in Table 3. The first PC accounted for Pb, Zn and above all Hg: it can be considered as the "pollution component", as it related to typical anthropic contamination parameters (Yongming et al. 2006). The main source of variability (i.e. information included in the data) is related to those metals that are collected in the first PC. The second PC was correlated to Cr, As and the extractable and total Ni. This component is related to the lithological information present in the dataset. In fact, such metals are naturally present in the soils of the studied area, as reported above.

The second PC explain a lower proportion of total variance, since due to the size and use of the area less variability can be associated with the soil metal composition. A strong correlation between Cr and Ni was also found by Bech et al. (2005). The third PC was only correlated to Cu (extractable and total), so it could be considered as an expression of the agricultural use of the soil. The fourth component was correlated to Cd and part of Hg.

In addition, multivariate analysis confirmed the strong correlation between total metals and their extractable counterparts.

Table 4 Principal		PC1	PC2	PC3	PC4	PC5
component loadings of	Cd	0.2269	0.4796	-0.6239	-0.2493	0.1021
properties and metal	Cr	0.6981	-0.2149	0.0984	-0.2532	-0.1952
content (main	Ni	0.6739	-0.1690	0.1790	-0.3489	-0.1043
correlations are reported	Cu	-0.1576	0.4510	-0.0150	-0.3427	0.5166
in bold)	Pb	-0.3448	0.8115	0.2156	-0.0847	0.0147
	Zn	0.1954	0.8484	0.1473	-0.1810	-0.0033
	Hg	-0.3223	0.3991	0.6652	-0.0028	-0.2654
	As	0.6248	0.0715	0.5127	-0.2816	0.0761
	OM	-0.1079	0.5840	-0.2735	0.3655	-0.1169
	CEC	0.3588	0.3891	0.0014	0.4778	-0.4153
	pН	-0.0845	-0.1286	0.4121	0.5119	0.6194
	Clay	0.8413	0.0893	0.1049	0.2857	0.0563
	Sand	-0.9166	-0.1408	0.0312	-0.2260	-0.1333
	Silt	0.7654	0.1732	-0.2160	0.0776	0.2046
	expvar	28.2%	18.7%	10.8%	8.9%	7.4%

Fig. 4 PC 1 and PC 2 loadings plot. Closely located factors are correlated. On the *x*-axis PC1: As, Ni, Cr, silt and clay; on *y*-axis PC 2: Pb and Zn



Metal content and physical chemical parameters

PCA was also used to examine the correlations between metal variables and the physical and chemical parameters of the soil. In this analysis extractable metal values were not included in the data processing, since they were redundant because of the strong correlation with the total values.

A total of five PCs were extracted, which accounts for 74% of the total variance, the loadings are shown in Table 4. The most important components were the first two, which explained 28.22%

and 18.70% respectively of the total variance. Figure 4 shows the loading plots of the first two PCs. Based on PC loadings, it is possible to see that the texture values (clay, silt and sand) were strongly correlated with PC1. The first PC explained the "lithological" part of the overall data because it was related to Ni, Cr and As (exactly like the second PC in the previous analysis reported in Table 3). The second PC was correlated to the "pollution component" as it grouped metals such as Pb and Zn. The correlation between the soil texture parameters and Ni, Cr and As, along with the first PC and the presence of

Distance from the MSWI	Orientation	Pb ext (orientation effective <i>p</i> value 0.021)	Pb tot (orientation effective <i>p</i> value 0.023)	Zn ext	Zn tot
Circle 1	NE	18.8	58.5	22.4	210
Circle 1	SW	5.14	27.9	6.68	121
Circle 2	NE	6.08	27.1	6.18	77.6
Circle 2	SW	4.45	29.3	7.18	113
Circle 3	NE	7.75	46.1	7.12	102
Circle 3	SW	4.35	26.6	3.93	92.6

Table 5 Effect of the distance from the MSWI and the orientation on the mean values of Pb and Zn in the soil

Circle 1 0–1,400 m (the first two circles from the MSWI in Fig. 2) from the MSWI, *circle 2* 1,400–2,700 m, *circle 3* 2,700–4,000 m, *NE* area of deposition of airborne carried by the prevalent wind

orthogonal components correlated to pollution, led us to hypothesise that there are two distinctive main groups of metals in the surveyed area: an anthropogenic metal group, due to the presence of human activities in the area (Pb and Zn) independently from the physical characteristics of the soil, as previously found (Bretzel and Calderisi 2006); and a lithogenic metal group, which represents the component of prevalent geological origin (Cr, Ni and As). The hypothesis is based either on the correlation mentioned above, between clay and Ni, Cr and As (Table 4 and Fig. 4), either on the different mobility, highest DTPA extractability of Pb and Zn, of the two groups of metals reported in Table 3 and highlighted in "Metals, total and extractable". These results are consistent with Biasioli et al. (2007) which found in urban areas Pb, Cu and Zn of anthropogenic origin, while Ni and Cr were explained by natural causes. The other possible sources of pollution, in addition to the MSWI, can be mainly vehicular traffic, intensive agricultural practices, industrial emissions, which correspond o the main activities of the areas. Cu correlated with OM, which can be explained by the affinity of Cu for OM.

Contamination plot

A pollution factor, consisting mainly of Zn and Pb was clearly identifiable from the first PCA elaboration. For this reason, only these two metals were analysed in order to check how the contamination had spread around the area.

The first check was achieved by taking into account the direction of the prevailing wind and the distance from the MSWI plant. The prevailing wind was from the south-west (SW) towards the north-east (NE). The distance from the incinerator was divided into three classes (circle 1 = 0-1,400 m, circle 2 = 1,400-2,700 m, circle 3 = 2,700-4,000 m). Each sampling point corresponded to one of these six classes. Thus, it was possible to calculate a sort of "rough estimate" of the mean pollution (Zn and Pb mean concentrations) for each class as reported in Table 5.

The highest mean concentration of Zn and Pb was found along the main wind direction (NE). The results were statistically significant only for Pb, although the values of Zn were evidently

different. The distance from the MSWI plant did not seem to create any difference in the concentration. Feng et al. (2000) found that distance did not have any influence on the concentration of metals in the vicinity of a MSWI plant, and nor did the direction of the prevailing wind. The lack of influence of the distance from the MSWI plant on Zn and Pb distribution could confirm that the presence of a strong anthropic activity in the area had a considerable effect, and created interferences that masked the effect of the MSWI. In fact, Zn and Pb are very often associated with urban pollution (Zhang 2006).

It is also important to note that the pollution was mainly distributed along a NE direction, towards the rural areas, in the opposite direction from the town of Pisa.

Conclusions

The results of this study showed that the main pollutants in the area around an MSWI plant in Pisa were lead and zinc. Other metals such as As, Cr and Ni were present as background origin. The increase in Pb and Zn, as pollutants in the soils from the MSWI plant, was confirmed by the results of the PCA and the values of the extractable fraction. The direction of the prevailing wind influenced the distribution of the pollutants (Pb and Zn), but the distance from the point source had no effect on the distribution of the pollutants. An analysis of the metal speciation showed that the highest number of contaminants was bound to the soil matrix, therefore not available for passage into the food chain. PCA was effective in describing and explaining the presence and the similarities or differences of the metals in soil, which were not evident from an examination of the raw data. PCA highlighted the relation between the finest part of the soil (clay + silt) and the lithogenic metals (Cr, Ni, As).

Grouping the samples into categories according to soil use was effective in terms of OM content and AS samples were the poorest (Fig. 3). Regarding the texture, the groups did not show any differences. The study showed that the pollution coming from other sources (urban and industrial activities, including traffic) interfered with the pollution coming from the MSWI. This would seem to indicate that it is not possible to quantify the contribution of the MSWI only by the monitoring of the soils, and that other sources need to be taken into account. This clearly has important implications for any town councils reviewing their plans with regard to MSWIs.

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