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EVALUATION OF TRACE METAL FLUXES TO SOILS IN THE HINTERLAND OF PORTO MARGHERA, INDUSTRIAL AREA: COMPARISONS WITH DIRECT MEASUREMENTS IN THE LAGOON OF VENICE

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Abstract. Trace metal (As, Cd, Cr, Ni, Hg, Pb) concentrations in soil samples collected around the Porto Marghera (Italy) industrial district (2-40 km) near the city of Venice were compared with direct measurements of atmospheric deposition measured at comparable distances from the same source. Concentrations of Cd and Pb in soils decreased exponentially with increasing distance from the source; less clear signals were detected for As, Cr and Ni. Significant differences were found among the soils, which were partially resolved when applying normalisation to their clay contents. Preliminary comparisons of fluxes of Cd and Pb derived from soil with direct deposition measurements show increasing values with longer integration times. Annual Cd and Pb flux values of one year of direct deposition were 5 to 10 times lower than mean annual fluxes derived from soils, integrating 50 to 100 years. Values range from ~ 0.1-0.4 to 1-2 mg $m^{-2}yr^{-1}$ for Cd, and from 3-18 to 50-100 mg $m^{-2}yr^{-1}$ for Pb. These results fit information on “historical” emission trends as recorded in sediments of the lagoon.

Keywords: atmospheric deposition, industrial fall-out, Lagoon of Venice**,** soil pollution, trace metals.

1. Introduction

Although several recent studies have revealed elevated concentrations of pollutants in the Lagoon of Venice (Di Domenico *et al.*, 1997; Di Domenico *et al.*, 1998; Wenning *et al.*, 2000), relatively little is understood about heavy metal conditions in inland coastal areas.

Within the framework of a monitoring program devoted to soil pollution in the vicinity of the Porto Marghera industrial district, located on the border of the Lagoon of Venice, 42 soil samples were collected in 1998 (Della Sala *et al*., 1999) and interim data on atmospheric fall-out of trace metals were provided by collecting bulk depositions from four stations inside the Lagoon of Venice (Fig. 1; Guerzoni *et al*., 1995).

Preliminary results of soil and atmospheric deposition studies have already been presented, showing clear decreases in some metals in soil with distance, connected with a main source in the industrial area (Di Domenico *et al*., 1998). Similar results come from bulk deposition sampling, which showed marked trends in atmospheric fluxes of pollutants with distance from Porto Marghera (Guerzoni *et al*., 1995; Rossini *et al*., 2001a).

The main aim of the present project was to assess comparisons between two projects related to heavy metals in soils and atmospheric deposition of metals. In addition, further evaluation of pedological parameters was carried out (Alloway, 1995; Baize, 1997), in order to identify better soils in an undisturbed state that have most likely been subjected to the industrial fall-out of the last 50-100 years.

2. Experimental

Of the 42 sites sampled, 34 were downgradient, i.e., at increasing distances from the central industrial zone, 5 were from the urban area of the city of Mestre (on the mainland opposite Venice) and 4 were in agricultural areas (Torre di Mosto, Staffolo). The background sites were chosen in areas far from possible local industrial sources and in good environmental condition (Giunta Regionale del Veneto, 1998). Four of the 42 sampling locations had not been plowed or significantly disturbed for several years (according to their pedological characteristics).

Atmospheric total deposition was collected by means of a bulk sampler (Mosello *et al.*, 1988), composed of a polyethylene bottle with a polyethylene funnel (surface area = 0.065 m^2) placed inside a PVC container. A total of 44 monthly deposition bulk samples was collected at one site near an industrial area (Dogaletto), one site in the city of Venice, and two sites in the southern and northern ends of the Lagoon (Rossini *et al.*, 2001a). Sampling was carried out following protocols adopted by the WMO (World Meteorological Organization), of which the CNR-ISMAR Institute is a scientific consultant (WMO/UNEP-MAP, 1998).

Soil physical characteristics and heavy metals (As, Cd, Cr, Ni, Pb) were quantified by the laboratory of the ARPAV Centro Agroambientale of Castelfranco Veneto (Italy). Standard methods established by the Italian Ministry of Agriculture (Ministero delle Risorse Agricole, Alimentari e Forestali, 1994) were followed for soil characterization determinations of grain size, organic matter, cation exchange capacity, pH and carbonates. Heavy metals were determined after acid sequence digestion of matrix aliquots and by atomic absorption spectroscopy.

Bulk deposition samples were filtered through 0.4-µm diameter Nuclepore© polycarbonate pre-weighed filters. Filtering was done with a Millipore© Sterifil unit, equipped with a pre-filter on the cover, to avoid contamination with ambient air. Sampling blanks were collected by washing the polyethylene funnel of the sampler with 500 mL of Milli-Q™ water (DDW), and laboratory blanks were also produced with DDW. Dissolved and particulate metal concentrations were determined by analysing filtered and residual fractions. After dissolution in an acidic mixture, the insoluble fraction was digested in Teflon bottles in a microwave digestion unit. Soluble and insoluble fractions were analysed for trace elements (Cr, Zn, Pb, Cd, As) by AAS and ICP mass spectrometry. All manipulations were conducted in a clean room equipped with a laminar flow bench. Extraction, clean-up and analytical procedures are extensively described in Rossini *et al*., 2001b.

Figure 1. Location of soil and atmospheric deposition sampling sites. (B = Background ~ 40 km; U = Urban < 5 km; T1, T2, T3 = Transects).

3. Results and Discussion

Some calculations were applied to soil data, in order to compare better soil and atmospheric deposition. The distances of the sampling sites were calculated from the hypothetical emission barycentre on the main point sources of atmospheric emissions from the Porto Marghera industrial area. Taking into account many studies stressing the importance of pedological development and soil rehashing for correct assessment of analytical soil data (Alloway, 1995; Kabata-Pendias and Pendias, 1984), we subdivided soil samples into homogeneous classes and applied normalisation on the basis of their clay contents. The complete set of soil samples was divided into undisturbed, agricultural and urban soils, all close to Porto Marghera (~4-5 Km), and compared with more distant background soils (Table 1).

Considerable differences in total Cd and Pb contents were detected between undisturbed and cultivated soils near Porto Marghera (<4 km), with values 1-2 times higher in undisturbed soils. No differences in total contents of Cr, Ni were seen, but the total As content in undisturbed soil was lower than in cultivated soil. Urban soil is enriched in Pb, and remote soils have the lowest Cd, Pb and As and the highest Cr and Ni.

Very interesting comparisons came from the clay-normalised data, in which differences between undisturbed and cultivated soils near the industrial area were completely reduced for Cd, and partially for Pb. This was not the case for Cr and Ni, in which the normalisation increased the differences, whereas As seemed unaffected. Normalisation in urban soils enhanced Pb enrichment. Values in remote soils became the lowest for all metals after clay normalisation.

The behaviour of Cd and Pb with normalisation suggested that the industrial (and perhaps also urban) pollution signals were evident at distances of <5 km, and is mainly transported by fine-grained aerosols, with some possible contribution from traffic lead, more independent of the transport carrier (i.e. coarser grain size).

Cr and Ni are geochemically important, and probably correlated more closely with the mineralogical phases of coarser grain sizes, so that normalisation increased differences instead of smoothing them.

As is unaffected by clay normalisation and presents regional geochemical variability in different areas (Bkg = ~10 mg/kg in the north, and ~25 in the south as reported by Scazzola *et al*., 2002, and 5-10 in lagoon sediments, according to the Water Management Authority of Venice, Magistrato alle Acque di Venezia, 1999). This fact, in connection with possible multiple sources (i.e., industry, glass-working, agriculture), made the behaviour of this metal difficult to explain.

TABLE I

Total and clay-normalised concentrations of As, Cd, Cr, Ni and Pb in soil samples, subdivided into homogeneous classes.

The normalisation procedure highlighted the strong industrial signals for Cd and Pb. Focusing on one of the three downwind transects (T1), the exponential decay ($y = y0 + a\ e^{-bx}$; where y = element concentration, y0 = background element concentration and x = distance) of Cd and Pb with increasing distance from the industrial district was revealed (Figure 2). Other metals (As, Cr, Ni) did not follow the same regular patterns of Cd and Pb, suggesting different multiple origins. In particular, concentrations of Cd and Pb collected downgradient from the central industrial zone were greater than background levels at close distances; beyond about 4-5 km, concentrations fell to background levels (Della Sala *et al.*, 1999). These data were normalized by clay contents in soil samples and are plotted as total and normalized heavy metal concentrations (Figure 2).

Figure 2. Plot of concentrations (mg/kg) of total Cd and Pb (A,C) and normalized Cd and Pb (B,D) in soil samples of transect 1 (T1) with distance (m) from Porto Marghera industrial zone. Line represents curve fit (B - r= 0.66; D - r=0.52).

For quantitative comparisons of fluxes, soil concentrations were converted into fluxes, with the equation:

$$\text{flux} = (C_i - C_{bkg}) * \delta * z / t$$

where C_i = sample concentration value, C_{bkg} = background concentration value, δ = bulk density, z = sample thickness and t = time interval.

For the sample concentration (Ci) it was considered the mean values of undisturbed sites and for the time interval it was considered that the sampled layer (15 cm) represents the last 50-100 years. This is reasonable, according to the pedogenetic structure, which shows no signs of disturbance, and the historical development of the industrial district (built in the 1920s).

These comparison were made for Cd and Pb by calculating the “excess” metal flux using background levels for the two metals derived from two different data sets. One was deduced from the profiles of two soil samples in which deeper pedological horizons were analysed separately. The other was the recent assessment of heavy metal background values in the inland coastal area of Venice (Scazzola *et al*., 2002). The values used were 0.4 mg/kg and 30 mg/kg for Cd and Pb, respectively.

TABLE II

Annual flux of Cd and Pb (mg m^{-2}) derived from soils and measured in atmospheric deposition.

Comparisons showed that "excess" fluxes of Cd and Pb, estimated from concentrations of trace metals in undisturbed soils minus background, were 5 to 10 times higher than recent measurements of atmospheric deposition. Annual "excess" Cd fluxes, as integrated for 50-100 years in soil, were 1-2 mg m^{-2} yr^{-1}, whereas measurements in the period 1998-1999 gave flux values of 0.1-0.4 mg m^{-2} yr^{-1}. The figures for Pb were 50-100 and 3-18 mg m^{-2} yr^{-1} for soil and atmosphere respectively. These results fit information on “historical” emission trends as recorded in sediments of the lagoon (Cochran *et al.*, 1998): emissions started in the 1920s-1930s, peaked in the 1960s-1980s, and are now declining, due to partial decline of industry, together with new national legislation on air emissions (D.P.R. 203/88 and others) and related abatement systems.

4. Conclusions

- Concentrations of Cd and Pb in soils decrease esponentially with increasing distance from the Porto Marghera industrial zone, and in the nearest soils (e.g., at distances <4 km from the petrochemical industry) there are differences between undisturbed and cultivated soils. As, Cr and Ni do not show clear trends with distance, nor do they present significant differences between undisturbed and cultivated soil, probably being more affected by geochemistry matrix.

- Preliminary comparisons of fluxes of Cd and Pb in soil with direct deposition measurements show increasing values with integration time. Annual Cd and Pb flux values of one year of direct deposition were 5 to 10 times lower than mean annual fluxes derived from soils, integrating 50 to 100 years. Values range from ~ 0.1-0.4 to 1-2 mg $m^{-2}yr^{-1}$ for Cd, and from 3-18 to 50-100 mg m^{-2} yr^{-1} for Pb. These differences are probably due to the historical atmospheric emission trends of the area.

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TABLE I

	Untouched (< 4.0 km)		**Agricultural (< 4.0 km)**		**Urban (< 5km)**		**Background (~ 40 km)**	
	mg/kg	*mg clay/kg.*	*mg/kg*	*mg clay/kg*	*mg/kg*	*mg clay/kg*	*mg/kg*	*mg clay/kg*
Cd	0.9 ± 0.1	3.4 ± 1.5	0.6 ± 0.2	3.5 ± 1.6	0.7 ± 0.2	3.4 ± 1.0	0.5 ± 0.1	1.2±0.1
Pb	53.± 34	175 ± 41	24 ± 10	127 ± 27	45 ± 37	236 ± 203	17 ± 4	42±9
Cr	17 ± 6	68 ± 11	18± 5	101 ± 32	23 ± 8	116 ± 49	26 ± 10	61±6
Ni	19.83 ± 6.03	74 ± 13	18 ± 5	103 ± 32	21± 5	104 ± 32	22± 11	50±13
As	12 ± 8	59 ± 15	17 ± 5	99 ± 38	19 ± 12	94 ± 46	8.4 ± 5	21±9

TABLE II

	Integration time yr	**Cd** mg m^{-2} yr^{-1}	**Pb** mg m^{-2} yr^{-1}
Atmosphere	1	0.1-0.4	3-18
Soil (excess)	50-100	1-2	50-100

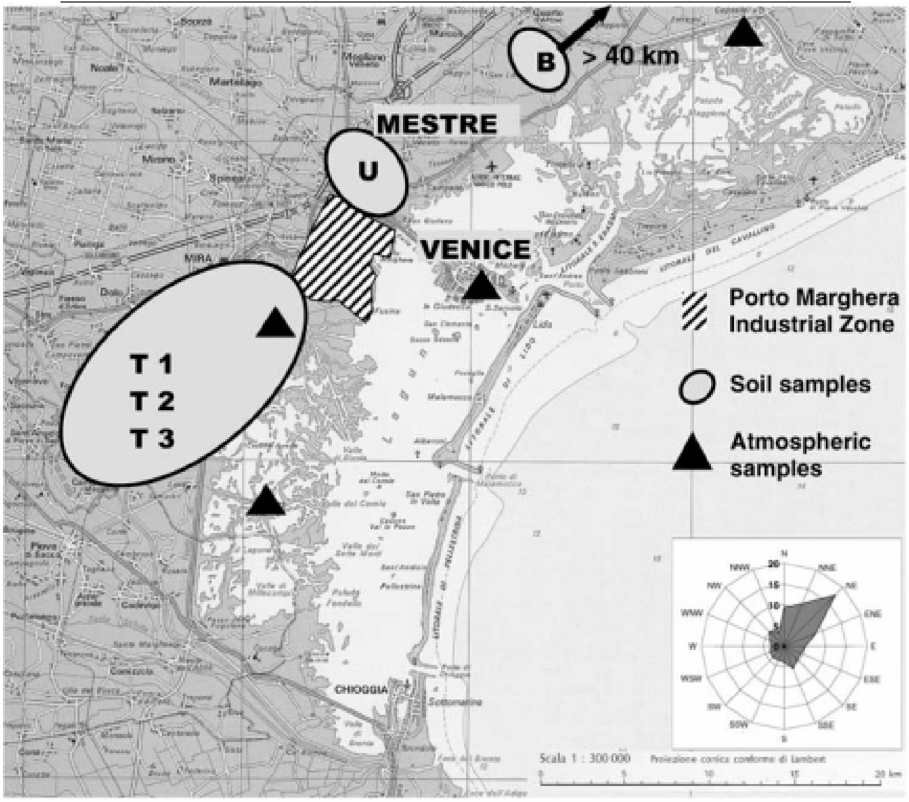

Fig. 1

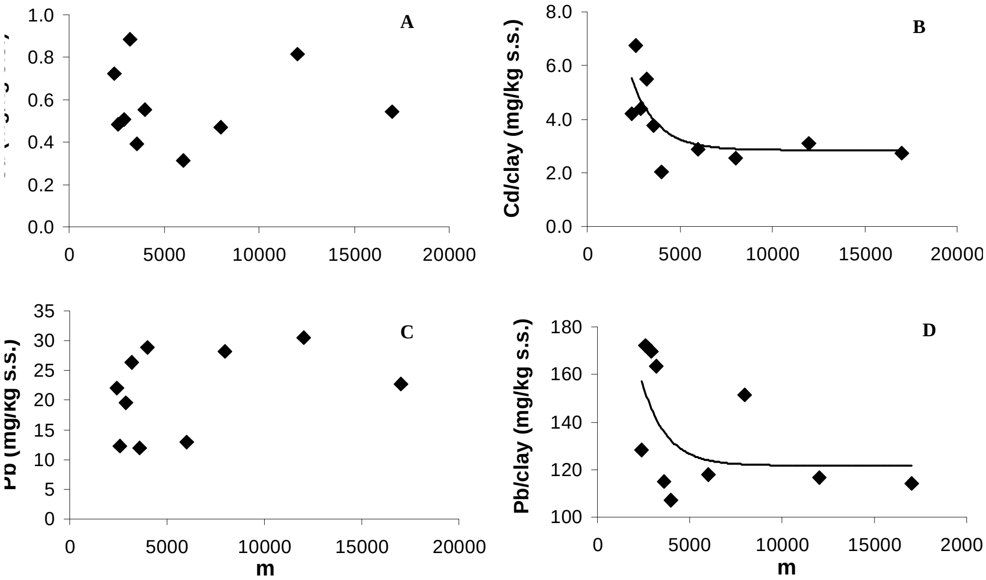
A
1.0
0.8
0.6
0.4
0.2
0.0
0
5000
10000
15000
20000
B
Cd/clay (mg/kg s.s.)
8.0
6.0
4.0
2.0
0.0
0
5000
10000
15000
20000
C
Pb (mg/kg s.s.)
35
30
25
20
15
10
5
0
0
5000
10000
15000
20000
m
D
Pb/clay (mg/kg s.s.)
180
160
140
120
100
0
5000
10000
15000
2000
m

Fig.2