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ORGANIC AND INORGANIC CONTAMINANT MONITORING IN SOIL: A CASE STUDY IN TREVISO PROVINCE

MONITORAGE DES CONTAMINANTS ORGANIQUES ET INORGANIQUES DANS LE SOL: UN CAS D'ÉTUDE DANS LA PROVINCE DE TRÉVISE

MONITORAGGIO DI CONTAMINANTI ORGANICI ED INORGANICI NEL SUOLO: UN CASO DI STUDIO IN PROVINCIA DI TREVISO

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Abstract

The present study concerns the environmental monitoring of a site that is close to the industrial area of Pederobba (Treviso province) which is characterized by the presence of a cement factory. Successively 43 soil samples were collected- including 26 surface samples and 17 deep ones. Each soil sample was analyzed and organic (PAHs, PCBs and PCDD/Fs) and inorganic (metals and metalloids) parameters were measured. Analytical results showed some values above contamination threshold levels in residential districts regarding PCDD/F, copper and cobalt.
Keywords: *soil; organic pollutants; metals*

Résumè

La présente étude concerne le monitorage de l'environnement effectué près de la zone industrielle de Pederobba dans la province de Trévise caractérisée notamment par la présence d'une cimenterie. Dans les phases successives ont été recueillis 43 échantillons de sol dont 26 en surface et 17 en profondeur sur lesquels ont été déterminés des paramètres organiques (HAP, PCB et PCDD/F) et inorganiques (métaux et métalloïdes). Les résultats d'analyse ont montré plusieurs dépassements des concentrations-seuils de contamination dans les terrains utilisés à des fins résidentielles pour les paramètres PCDD/F, cuivre et cobalt.
Mots-clés: *sol; polluants organiques; métaux*

Riassunto

Il presente studio riguarda un monitoraggio ambientale condotto in prossimità dell'area industriale di Pederobba in provincia di Treviso caratterizzato in particolare dalla presenza di un cementificio. In fasi successive sono stati raccolti 43 campioni di suolo di cui 26 in superficie e 17 profondi su cui sono stati determinati parametri organici (IPA, PCB e PCDD/F) ed inorganici (metalli e

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metalloidi). I risultati analitici hanno evidenziato alcuni superamenti delle concentrazioni soglia di contaminazione per i terreni ad uso residenziale per i parametri PCDD/F, Rame e Cobalto.
Parole chiave: *suolo; inquinanti organici; metalli*

Introduction

During 2008 and 2009 an environmental monitoring was carried out near an industrial area in Pederobba (Treviso). Concerning soil, the monitoring activity was about sampling and analysing soil samples in order to detect some organic and inorganic substances in the municipal area between Pederobba and Onigo villages.
Soil has a memory effect concerning pollutant inputs. Organic substances, particularly those with higher lipophilicity, bind to soil organic carbon and stay quite stationary once they are adsorbed; limited removal and quite long half-life of some of them cause the further inputs to accumulate time after time. The same process occurs to metals: soil behaves as an accumulating matrix where metals bind to organic matter and clay showing a low mobility. This happens particularly under basic pH conditions, typical of the investigated areas, which tend to determine a very low solubility.
This behaviour allows to recognise, by comparing surface and deep concentrations, metal concentrations due to "pedo-geochemical background content", that is typical of minerals from which soil was originated, and "background content" which summarizes the natural content and the concentration related to human activities. These processes are due to particulate deposition, but also to common use of pesticides and fertilizers in agriculture.
The investigated area is mainly located on high plain soils formed on Piave River alluvial deposits of different ages (Fig. 1).

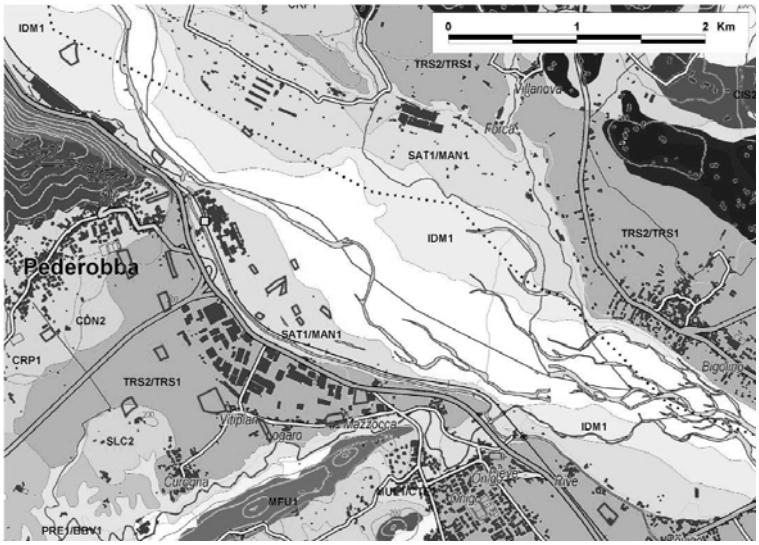

Figure 1

Soil map of the investigated area with indication of sampled sites.

Recent soils are separated from older ones through a slope of about 30 meters; on the higher terrace of Pleistocene fluvioglacial deposits, soils show highly differentiated profile with rubified horizons of illuvial clay accumulation. The lower terrace is close to the actual riverbed and it is made of recent depositions (Holocene): here the most common soils are shallow, with medium or coarse texture, with plenty of extremely calcareous coarse fragment, and rapid drainage.

Materials and methods

At the beginning the location of sites (sites 1-14) aims to cover uniformly the area around the manufacturing activities according to a grid which was as regular as possible according to the presence of an industrial zone, of urbanized areas and high traffic roads (Fig. 2). First locations included a site located in the north (n. 1) and a second one in the west (n. 13), both located in areas which were less affected by industrial source pollutants.

Figure 2

Location of sampled sites. The sites interested by samples collection for determination of organic parameters are highlighted in white (Ortofoto TerraItaly ™ - © Copyright Compagnia Generale Riprese Aeree).

An additional criterion was to limit soil variability as much as possible in order to reduce the effect due to the natural content at least for metals.
Following the methodology established by ISO 19258/2005, a surface sample was collected in each site (within the ploughed horizon, about 40 cm deep, or below the turf, between 5 and 20 cm for non-ploughed soils), representative of the usual content, and a deep one (about 60 cm deep, or at least below the ploughed horizon) representative of the natural content. In five of these sites (nn. 1, 4, 8, 11, 13) rates of surface samples were used for organic substances determination.
To verify the exceeding for the parameter PCDD/Fs occurred at the site n. 11, the same site and a new next one (n. 15) were sampled. In this step a third site (n. 16)

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moved south-east was added. In these three sites, superficial and deep samples were collected.
The last monitoring step involved further eight sites, some located around sites n.11 and 15 (nn. 17, 21, 22, 23), some at similar distances from the cement factory stack, but in different directions than the sites 11 and 15 (nn. 20, 24). Site n.14 was sampled again in order to detect also organic substances. Further more two sites (nn. 18,19) were added that were suspected to be involved in a waste combustion activity in the past.
The total number of collected and analyzed samples during the whole survey was 43, including 26 topsoil (including two repeats) and 17 subsoil samples. For all of them determinations on soil standard parameters and inorganic parameters were performed. 22 soil samples were analyzed for organic pollutants (17 in the topsoil - including a repeat - and 5 in the subsoil).
Each site is approximately 1 hectar wide. Samples were collected following a systematic scheme as specified in ISO 10381-5:2005.
The following parameters were detected:
• standard chemical and physical soil parameters: texture, pH, organic carbon, cation exchange capacity (CEC), total carbonate;
• inorganic parameters: As, Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Zn, Tl, V, F^-, CrVI;
• organic parameters: PCDD/Fs, PCBs, PAHs and HCB.
Soil samples were dried at room temperature and then sifted with 2 mm. Before metal content determination in order to avoid possible sample contamination, the fine fraction was grounded through a mill with agate mortar and only the smaller fraction (< 0.2 mm) was analyzed; results have been extended to the whole sample.
Soil standard parameters and metals were detected in the laboratory of the Regional Laboratory Department of ARPAV in Treviso.
Concerning organic parameters, concentrations are calculated as required by Legislative Decree no. 152/06: samples should be free of the fraction bigger than 2 cm (to be excluded on the field) and determinations should concern only the fraction wich is smaller than 2 mm.
The concentrations refer to total dry material, including coarse fragments (up to 2 cm). Organic compounds detections were performed by the Interuniversity Consortium "Chemistry For The Environment" (INCA-VE). Results were compared with values reported in Table 1 Annex 5 to Part IV of Title V of the Legislative Decree no. 152/06 which represent contamination threshold levels in soil and subsoil, related to site specific land use; in particular column A shows levels related to residential land use while column B refers to commercial and industrial land use. Applying the precautionary principle column A is generally the reference also for agricultural areas, even though these are not considered by law.
Organic parameter concentrations which were below the detection limit were considered equal to 0 while for other parameters they were considered equal to half the detection limit.

Results and discussion

Analytical results are presented in the tables 1 and 2.
As shown in the table 1, concerning inorganic parameters, there are some exceeding of contamination threshold levels for residential land use.

Table 1- *Summary table of inorganic parameters; values greater than threshold levels are bold underlined characters. Data refer to dry material up to 2 mm size.*

Site	depth	Fe	Cd	Co	Cr	Cu	Ni	Pb	Zn	Mn	As	Sb	Hg	Se
	cm	g/kg dw	mg/kg dw											
1	2-15	6,3	<0.5	1,8	<5.0	10	<5.0	<5.0	52	200	2,7	0,37	<0.05	<0.2
2	15-40	27,1	0,59	**27,0**	45,0	80	45,0	45,0	99	2500	11,5	0,99	0,05	0,25
2	50-70	29,6	<0.5	**20,0**	45,0	49	48,0	30,0	92	2000	10,0	0,66	<0.05	0,20
3	10-30	24,9	0,5	12,3	37,0	**130**	33,0	40,0	94	1500	9,0	0,73	0,08	0,28
3	50-80	27,1	<0.5	12,8	39,0	43	34,0	24,0	75	1400	8,9	0,85	<0.05	0,21
4	10-30	25,6	<0.5	13,1	36,0	**130**	32,0	37,0	87	1500	9,9	0,65	0,07	0,27
4	50-60	40,5	<0.5	15,8	58,0	41	51,0	25,0	96	1700	14,1	0,73	0,05	0,30
5	15-30	24,2	<0.5	15,3	37,0	85	38,0	43,0	84	1500	8,5	0,71	0,07	0,21
5	50-80	29,7	<0.5	15,2	42,0	44	44,0	23,0	83	1500	10,1	0,56	0,05	<0.2
6	20-40	27,4	<0.5	12,6	41,0	63	33,0	34,0	76	1400	9,4	0,73	0,05	0,28
6	60-80	35,1	<0.5	13,6	52,0	29	43,0	24,0	79	1600	11,9	0,62	<0.05	0,28
7	15-30	27,2	<0.5	11,7	42,0	73	34,0	40,0	99	1400	10,0	0,75	0,10	0,32
7	60-80	32,9	<0.5	13,5	48,0	37	40,0	29,0	83	1500	12,7	0,66	0,06	0,27
8	10-30	25,6	<0.5	10,9	40,0	68	31,0	33,0	74	1200	10,6	0,71	0,06	0,31
8	50-70	35,7	<0.5	13,7	52,0	29	43,0	23,0	77	1400	12,3	0,66	<0.05	0,29
9	10-30	27,4	<0.5	10,7	38,0	55	29,0	30,0	80	1200	9,6	0,75	0,06	0,29
9	60-70	38,4	<0.5	12,9	49,0	33	42,0	24,0	85	1500	12,6	0,65	0,05	0,33
10	10-20	12,1	<0.5	3,9	12,4	62	10,3	21,0	120	300	6,2	0,67	0,08	<0.2
11	10-20	11,2	<0.5	3,6	11,9	24	10,0	15,8	99	280	5,7	0,59	0,10	<0.2
11	5-20	11,5	<0.5	3,8	11,8	27	10,4	17,1	99	300	5,6	0,34	0,10	<0.2
11	45-70	11,9	<0.5	3,7	12,8	23	10,5	14,2	96	290	5,5	0,40	0,08	<0.2
12	15-40	29,9	<0.5	**25,0**	48,0	51	49,0	33,0	89	2000	10,2	0,61	0,05	0,24
12	60-80	35,1	<0.5	**21,0**	58,0	44	61,0	21,0	100	1600	10,5	0,61	0,05	0,22
13	20-40	27,5	0,9	**34,0**	63,0	**120**	83,0	47,0	110	3400	9,6	0,71	0,09	0,32
13	50-70	29,7	0,79	**35,0**	66,0	57	97,0	33,0	92	3300	8,8	0,44	0,07	0,22
14	10-30	26,0	0,54	15,7	39,0	**170**	37,0	43,0	110	1700	11,4	0,87	0,14	0,24
14	50-60	31,5	<0.5	16,3	51,0	63	45,0	26,0	94	1500	11,9	0,68	0,07	0,20
15	10-30	11,5	<0.5	3,5	11,4	28	9,3	16,1	95	290	5,4	0,31	0,07	<0.2
15	45-75	12,0	<0.5	3,8	11,6	29	10,1	16,4	97	290	5,7	0,38	0,09	<0.2
16	10-30	27,5	<0.5	11,4	43,0	32	33,0	46,0	85	1300	9,0	0,53	0,05	0,23
16	50-70	38,5	<0.5	13,7	53,0	26	44,0	23,0	84	1500	11,8	0,52	<0.05	0,27
Threshold level			2	20	150	120	120	100	150		20	10	1	3
mean		25,8	0,32	13,8	38,6	56,6	36,5	28,4	89,8	1389	9,4	0,63	0,06	0,22
median		27,4	0,25	13,1	42,0	44,0	37,0	26,0	92	1500	9,9	0,66	0,06	0,24
min		6,3	0,25	1,8	2,5	9,7	2,5	2,5	52	200	2,7	0,31	0,03	0,10
max		40,5	0,90	35,0	66,0	170	97,0	47,0	120	3400	14,1	0,99	0,14	0,33
s.d..		9,2	0,17	8,3	17,1	37,1	20,7	10,8	13,0	791	2,7	0,16	0,03	0,08
n.		31	31	31	31	31	31	31	31	31	31	31	31	31

The involved parameters are cobalt and copper respectively in the sites 2, 12, 13 and 3, 4, 13, 14. Results refer to dry material up to 2 mm size, but soils are so rich

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in skeleton that values calculated including coarse fragment should be within law limits.

Table 2 - *Summary table of organic parameters; values greater than threshold levels are bold underlined characters. Data refer to total dry material including coarse fragment (up to 2 cm).*

site	depth cm	step	PCDD/Fs ng/kg dw	PCBs µg/kg dw	HCB µg/kg dw	PAHs µg/kg dw
1	5-15	I	1.0	1,98	0,05	100,7
4	10-30	I	2.3	1,15	0,42	109,1
8	10-30	I	0.8	1,07	0,49	166,3
11	5-20	I	**18,0**	2,77	0,14	256,4
11	5-20	II	**23,9**	3,20	0,18	518,2
11	45-70	II	9,3	2,63	0,09	315,0
13	20-40	I	0,6	1,09	0,04	97,4
14	5-20	III	**10,5**			425,5
15	10-30	II	**17,6**	2,49	0,18	777,4
15	45-70	II	**14,5**			279,1
16	10-30	II	1,9	2,26	0,39	121,9
17	10-30	III	0,9			255,8
18	0-10	III	3,5			150,1
19	0-10	III	4,1			187,8
20	0-20	III	1,4			420,4
21	0-15	III	0,3			348,0
21	30-50	III	0,7			510,2
22	10-30	III	**29,8**			314,7
22	50-70	III	0,5			438,7
23	10-30	III	1,0			185,0
23	60-90	III	0,2			256,7
24	0-10	III	2,6			247,6
Threshold levels			10	60	50	10000
mean			6,6	2,07	0,22	294,6
median			2,1	2,26	0,18	256,6
min			0,2	1,07	0,04	97,4
max			29,8	3,20	0,49	777,4
SD			8,7	0,80	0,17	168,4
N.			22	9	9	22

Cobalt presents high values in both surface and deep horizons. This shows a natural contribution in the content of this metal; this statement is corroborated by the

available data in Treviso province which show some values above the limit of column A (20 mg/kg dw) in both superficial and deep samples in soils of hills and pre-Alpine reliefs districts. Background values (95° percentile of the values found in surface samples) for these districts are equal respectively to 32 and 39 mg/kg dw.

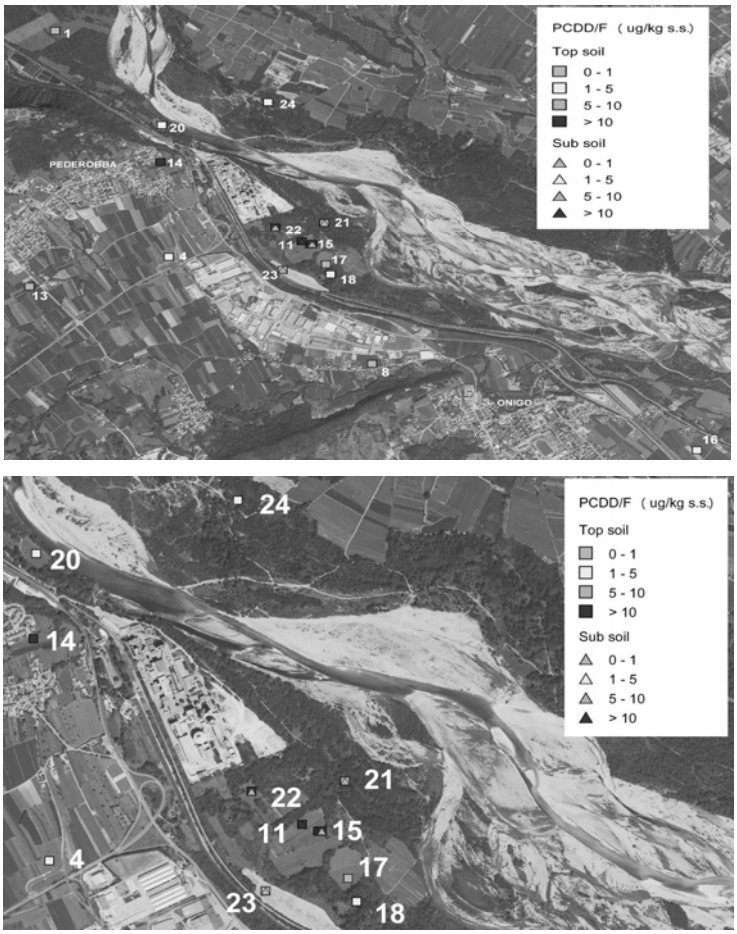

Figure 3

Location of sites sampled with the results representation for PCDD/Fs, above there is a representation of the whole investigated area, below there is the area affected by the higher values. (Ortofoto TerraItaly ™ - © Copyrigh Compagnia Generale Riprese Aeree).

Copper concentrations which are above the threshold level (120 mg/kg dw) concern only surface samples. In the whole data set surface values, except for site n. 15, are higher than deep ones. This behaviour emphasizes the anthropic contribution which is likely due to the widespread use of plant protection products as copper sulphate connected to the wide presence of vineyards. Concerning other inorganic parameters there are no particular circumstances: for some metals (Pb, Zn, Hg, Cd, Sb) surface horizons have an average content higher than deeper horizons, probably because of light enrichment due to anthropogenic phenomena analogous to what is observed in the remaining province land.

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Regarding the parameter PCDD/Fs there are some exceeding of the threshold level ($1*10^{-5}$ mg I-TEQ/kg dw) that specifically relate to the sites 11, 14, 15 and 22 (Fig. 3). In the site 15 both surface and deep horizons show high values (respectively 17.6 and 14.5 ng I-TEQ/kg dw). The highest value was detected in the site n. 22 (29.8 ng I-TEQ/kg dw) in the surface horizon.
High values in deep horizons were detected in sites n. 11 and n. 15. This could be due to past deep plowing, bearing in mind that these substances have a very low mobility in soil. For site 14, the deep horizon could not be sampled because of the high gravel content. In all the other samples concentrations vary between 0.2 and 4.1 ng I-TEQ/kg dw. Data refer mostly to surface horizons; it was possible to collect deep sample only in sites 21 and 23.
Regarding PAHs, detected values do not show critical situation (mean 294 μg/kg dw, range between 97.4 and 777.4 μg/kg dw) and are always well below the threshold level (10 mg/kg dw).
Regarding PCBs and HCB, data refer to samples collected during the first two sampling step. Values (PCBs: mean 2.07 μg/kg dw, range between 1.07 and 3.20 μg/kg dw, HCB: mean 0.22 μg/kg dw, range between 0.04 and 0.49 μg/kg dw) are always well below threshold levels.

Conclusions

Many different factors are influencing soil contamination in the investigated area. Higher pressure is maybe due to air emission from an industrial site but fall out direction is not easily predictable. A monitoring network of soil at regional scale has to be set up taking into consideration relationship between industrial and agricultural pressures.

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