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Application of Contamination Indexes on Different Farming Soils

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The continuous impact that soil suffers due to human activities (deficient planning, excessive use of fertilizers and pesticides, waste water irrigation, etc.), makes necessary to take in account actions of control and regeneration of it. These circumstances have promoted extensive studies, mainly focused on the quantization and distribution of heavy metals and pesticides in soils, around urban and industrial point sources (Leita et al., 1991). However, there is not coincidence of criteria about at what level the metal in soils could be considered, initially, toxic for plant growth. This is reflected, actually, by the existing legislation that is, often, insufficient and differs markedly between countries. Facing to obtain information about soil status of heavy metal contamination and its potential toxicity, several indexes have been formulated.

In 1970 the Agricultural Development and Advisory Service of England and Wales, based on field and lab experiences (Chumbley, 1971; Webber, 1972), proposed a general criterion about the relative toxicity of Cu, Ni and Zn. This criterion assumes that the presence together of these metals potentiates its toxic effects and, its validity is restricted only for pH values higher than 6.5 (Jones and Jarvis, 1981). This criterion was named "Zn equivalent" and the formula is: Zn equivalent (mg/kg dry matter) = Zn + 2Cu + 8Ni. It is considered that, soils with values of Zn equivalent above 250 mg/kg are potentially toxic.

The "Zn/Cd ratio" is based in the antagonistic effect of Zn on Cd assimilation by plants. Diamant (1979) asserted that this ratio must be higher than 100. However, Chaney et al. (1981) considered that it must be higher than 200, although estimated a value of 1000 the optimum to obtain an effective antagonism between Zn and Cd in plants. Both indexes, the Zn Equivalent and the Zn/Cd ratio, were developed in basis to its application on agricultural soils amended with sewage sludge, to obtain an idea about its level of contamination (Jones and Jarvis, 1981).

The third index applied, the extactable/total ratio, can be useful to obtain information about the bioavailability and mobility of these elements in soil, and to know their proportion available for adsorption by plants. In this paper, these

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indexes have been applied to provide a basis for comparison, about heavy metalcontamination, between the different soils and zones.

MATERIALS AND METHODS

The area composed by the L'Horta and Ribera Baixa regions was selected for this work. In particular, the marsh of the Natural Park of La Albufera (Valencia, Spain) and the zones of vegetables and fruits crops around it. This area shows a high industrial concentration and road network.

For a best understanding of the degree and distribution of contamination in the surveyed territory, it has been divided in three big areas that are subdivided in 8 zones.

La Albufera and marsh area comprises all the marsh and rice farming of the Natural Park. It is subdivided in 4 zones by virtue of proximity to potentially points of contamination (industries, cities, roads..). The Zone 1 is characterized by the marsh to the South-East of La Albufera. It is bounded by the West for the urbanized area near the sea, and by the East for Sueca and the road N-340. Zone 2 covers the marsh to the South-West of La Albufera, bordered by the West and South for vegetables and citrus crops. Zone 3 occupies the North-East of the marsh, the lake of La Albufera is its southern limit. And Zone 4 is located at North-West of the lake, is with the previous one, the nearest zone to the industrial belt of Massanasa-Catarroja.

The meadow area comprises the coastal strip, with the dunes border (Zone 5).

The interior area surrounds the first four zones and are fully occupied of vegetables and citrus crops. In it, Zone 6 presents in all its extension citrus crops, which bear particular treatments with fertilizers and pesticides. Zone 7 cover the vegetable farming and orchards. Zone 8: groups of soils with natural vegetation, near contaminant points.

Over a hundred of samples corresponding to surface and deep horizons of soils, were collected. The location of the surface samples taken is indicated by their identification number in Table 1.

All the analytical material was conditioned in a bath of 20% HNO_3, a period of 12 hours, and washed three times with distilled-deionized water. The soil samples were air-dried, passed through a 2 mm sieve and homogenized in an agate mortar, prior the treatment with reagents.

The total content of metals in soil was determined by HNO_3-$HClO_4$ acid digestion and later solution of the residue with 6M HCl (Ministry of Agriculture, 1981). The determination was carried out by flame atomic absorption spectrometry (FAAS), employing an air acetylene flame and a spectrometer Perkin Elmer 2500. In the case of cadmium, the additions method (Andreu, 1993) was used and its

Table 1. Values of the Contamination indexes for the analyzed surface samples.

		Sample No.	Zn Equiv. (mg/kg)	Zn/Cd Ratio	EXTRACTABLE/TOTAL RATIO (%) Cd	Co	Cr	Cu	Ni	Pb	Zn
ALBUFERA AND MARSH AREA	ZONE 1	**91**	360.01	86.76	4.91	2.53	0.53	28.36	1.96	8.95	8.10
		94	253.00	62.11	3.70	2.77	1.18	14.21	3.34	5.45	1.25
		98	236.18	148.80	25.86	1.21	0.27	18.38	2.14	12.08	4.59
		100	378.62	93.02	17.04	0.62	0.74	25.21	2.13	12.46	7.31
		119	375.99	167.01	32.88	0.61	0.24	23.31	0.61	10.95	2.42
		121	336.60	126.94	13.08	0.45	0.47	20.94	1.34	12.63	3.86
		Average	**323.40**	**114.11**	**16.25**	**1.37**	**0.58**	**21.74**	**1.92**	**10.43**	**4.60**
	ZONE 2	**102**	369.89	124.97	19.06	0.45	0.37	21.28	1.57	9.96	4.53
		104	232.52	98.61	36.40	1.19	0.59	21.30	1.07	15.53	6.78
		251	253.60	46.80	13.85	0.52	0.37	18.70	0.60	7.71	8.46
		253	462.03	112.34	17.23	0.54	0.26	12.56	1.41	15.06	8.11
		Average	**329.51**	**95.68**	**21.63**	**0.69**	**0.40**	**18.46**	**1.16**	**12.07**	**6.97**
	ZONE 3	**138**	481.17	127.55	26.96	1.00	0.20	32.13	5.99	28.44	15.25
		142	560.41	217.30	30.95	0.96	0.16	28.53	5.36	26.77	16.92
		144	404.83	129.61	47.81	0.82	0.29	22.01	2.79	15.43	6.45
		606	399.83	193.11	38.84	0.58	0.21	33.54	7.44	18.48	13.19
		Average	**461.56**	**166.89**	**36.14**	**0.84**	**0.22**	**29.06**	**5.40**	**22.28**	**12.95**
	ZONE 4	**140**	451.84	104.28	29.72	0.84	0.41	29.60	6.19	15.83	14.73
		146	487.53	137.58	29.82	0.91	0.15	30.99	1.89	18.70	13.76
		148	403.94	133.21	35.71	1.42	0.13	29.13	1.52	18.69	10.36
		Average	**477.78**	**125.03**	**31.75**	**1.06**	**0.23**	**29.91**	**3.20**	**17.74**	**12.95**

Table 1. Values of the Contamination indexes for the analyzed surface samples. (Cont.)

					EXTRACTABLE/TOTAL RATIO (%)						
		Sample No.	Zn Equiv. (mg/kg)	Zn/Cd Ratio	Cd	Co	Cr	Cu	Ni	Pb	Zn
DUNES	ZONE 5	**642**	180.32	263.60	22.59	0.61	0.28	2.79	0.00	7.57	2.53
		644	217.59	441.44	35.93	0.61	0.41	5.69	1.33	12.24	4.02
		Average	**198.95**	**352.53**	**29.27**	**0.61**	**0.35**	**4.24**	**0.67**	**9.90**	**3.28**
INTERIOR AREAS	ZONE 6	**87**	292.01	73.97	10.46	1.41	0.41	21.26	4.78	9.56	10.02
		106	321.18	111.74	27.72	2.16	0.69	16.37	3.50	13.65	17.75
		128	353.78	455.01	27.90	3.57	0.56	18.80	4.35	6.56	7.12
		257	105.46	41.72	2.39	0.36	1.14	6.52	3.68	3.84	1.14
		263	280.93	111.24	9.27	3.03	0.26	8.80	3.41	7.91	1.67
		621	298.52	55.71	39.30	2.21	0.35	18.65	3.76	35.46	4.74
		626	313.25	247.77	31.62	0.44	0.21	10.41	1.91	15.18	1.71
		Average	**280.73**	**156.75**	**21.24**	**1.88**	**0.56**	**14.41**	**3.63**	**13.17**	**6.31**
	ZONE 7	**83**	234.47	82.90	10.65	2.05	0.91	17.86	4.41	8.55	12.18
		612	356.66	208.01	29.47	1.13	0.26	19.40	1.71	19.38	11.63
		617	344.75	284.72	37.21	1.57	0.37	16.50	2.59	15.44	5.40
		624	299.65	110.80	39.84	1.83	0.34	7.45	1.14	13.29	9.22
		Average	**308.88**	**171.61**	**29.30**	**1.66**	**0.48**	**15.31**	**2.46**	**14.16**	**9.61**
	ZONE 8	**162**	369.62	113.32	16.37	0.57	0.61	12.64	1.39	13.56	10.05
		244	234.53	71.57	17.62	1.58	0.64	4.80	2.59	4.11	1.38
		Average	**302.08**	**92.45**	**17.00**	**1.07**	**0.63**	**8.72**	**1.99**	**8.84**	**5.72**

determination was carried out by graphite furnace atomic absorption spectrometry (GFAAS).

Extractable fraction of metals was obtained by shaking 8 g of air-dried soil (size fraction <2mm) with 35 ml of 0.05M EDTA at pH=7, 1:4 soil/extractant ratio, during 2 hours. The procedure was performed according to the proposed method of the Dept. of Environmental and National Water Council (1983). Cu, Ni, Pb and Zn were determined by FAAS and the rest of elements by GFAAS, in the same measurement conditions as the total content. Four repetitions were realized in each analysis for all samples.

The determinations of physical and chemical characteristics of soils were carried out according to the official methods of the Ministerio de Agricultura (1974).

RESULTS AND DISCUSSION

Mean values on chemical and physical characteristics of soils representatives of each zone are given in Table 2. In Table 3, the average values per zones of total content and extractable fraction of the metals are reported. The index values of the surface soil samples grouped by zones is showed in Table 1.

Total contents of the studied metals in the samples are according to the values reflected in the bibliography for natural and farming soils (Aller and Deban, 1989; Crisanto and Lorenzo, 1993), except in the cases of Cu and Zn whose values exceed the normal levels in soils, 20mg/kg of Cu (Holynska et al., 1988) and 7-13 mg/kg of Zn (Dressler et al., 1986; Juste and Solda, 1989).

Lower levels of extractable fraction of the metals are observed in the samples comparing with the values reported by several authors for similar soils (Klessa et al., 1989; Berrow and Burridge, 1990). Cu and Zn, as in the total content occurs, present values higher than the consulted bibliography presents, 0.3-3 mg/kg of Cu (Xian, 1987; Burridge and Hewitt, 1987) and 1.5 mg/kg of Zn (Archer and Hodgson, 1987; Aller and Deban, 1989).

Generally, all samples present values of Zn equivalent higher than 200 mg/kg, with an average value of 285.80 mg/kg. Marsh zones present the most important levels, mainly zones 3 and 4, except chromium, which reach maximum values of the index in the citrus zone.

Maximum values appeared correspond to surface horizons (Ap_1 and Ap_2) of a marshy soil of zone 3, 550.41 and 535.82 mg/kg respectively. Chaney (1973) reflects values near 3500 mg/kg on agricultural soils of England, amended during five years with sewage sludge. Errecalde et al. (1991), in a study of these indexes on soils with different farming in the North of the region of Valencia, report lower values of Zn equivalent for soils supporting citrus (163-200 mg/kg) and others with rice farming (260 mg/kg). The sequence of index values for the metals studied is Cd>Cu>Pb>Zn>Ni>Co>Cr.

Table 2. Mean values of physical and chemical characteristics of surface horizons in the different zones.

	Albufera and Marsh				Dunes	Interior		
ZONES	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Soil moisture (%)	3.9	3.2	2.4	4.7	0.5	1.4	0.9	2.3
pH (H_2O)	7.5	7.5	7.4	7.2	8.0	7.9	7.6	7.9
E.C. (S/m)	1.95	2.04	4.30	5.63	0.44	0.94	0.47	0.58
$CO_3^=$ (%)	45.65	33.84	33.15	46.89	22.40	36.19	33.42	29.29
M. O. (%)	2.63	2.75	3.78	6.13	0.46	0.89	1.35	3.31
C.E.C. (meq/100g)	18.97	17.66	21.67	21.13	2.06	9.57	13.11	13.92
Mg (meq/100g)	5.70	5.49	3.19	5.60	0.16	1.62	0.89	1.23
Na (meq/100g)	1.58	1.16	5.92	12.29	0.04	0.40	0.07	0.13
K (meq/100g)	0.63	0.67	0.37	0.66	0.01	0.35	0.20	0.48
Ca (meq/100g)	11.05	10.32	12.19	2.58	1.85	7.25	11.91	12.09
N total (%)	0.23	0.19	0.26	0.37	0.08	0.09	0.09	0.23
N min. (mgN/100g)	1.13	5.00	1.45	1.63	1.28	1.46	0.95	1.39
P (mgP_2O_5/100g)	4.26	15.89	9.42	18.90	0.08	1.70	3.50	0.11
Str. Est.(%)	8.1	6.5	9.3	17.5	4.1	0.6	8.8	14.9
Clay (%)	32	26	38	25	1	19	20	13
Sand (%)	16	23	9	15	72	50	47	55
Silt (%)	52	51	53	60	27	31	33	32

E.C.: Electric conductivity. **O.M.:** Organic matter. **C.E.C.:** Cation Exchange Capacity. **$CO_3^=$:** Total carbonates. **P:** Available Phosforous. **N total:** Total Notrogen. **Str. Est.:** Structural estability.

Table 3. Average values of the studied heavy metals (in mg/kg) per zones.

	ZONES							
	1	2	3	4	5	6	7	8
				EXTRACTABLE FRACTION				
Cd	0.05	0.12	0.15	0.15	0.05	0.07	0.09	0.05
Co	0.14	0.07	0.14	0.14	0.04	0.10	0.11	0.12
Cr	0.07	0.04	0.05	0.03	0.10	0.08	0.05	0.07
Cu	4.96	4.27	7.43	11.29	0.54	1.80	2.45	1.31
Ni	0.50	0.31	1.51	1.07	0.15	0.52	0.57	0.56
Pb	3.67	6.05	11.52	10.80	1.93	3.49	4.09	3.29
Zn	1.44	3.29	7.98	7.67	1.30	1.56	4.23	1.43
				TOTAL CONTENT				
Cd	0.49	0.54	0.49	0.49	0.14	0.43	0.33	0.29
Co	9.67	11.13	15.00	11.11	6.74	8.09	8.49	10.30
Cr	11.44	9.34	22.97	17.15	30.35	9.72	10.51	9.74
Cu	21.67	22.36	27.05	36.81	14.85	14.45	14.82	14.68
Ni	25.36	25.93	37.07	36.16	13.23	19.23	21.08	26.14
Pb	42.29	47.60	53.15	55.23	28.14	36.89	36.42	38.03
Zn	45.24	56.12	85.72	57.64	46.93	44.77	51.56	25.97

According to the more recent criteria about Zn/Cd ratio (values$>$ 1000) all samples correspond to polluted soils, even taking as reference the Chaney criteria more than 70% of samples could be included. Only if the value of 100 is taken, recommended by Diamant (1979), a smaller percentage is obtained (30% of the samples). The average value of the samples (148.24) can reflect approximately the contamination stage of the area.

The lower values appear in zone 1 (33.09), and the higher correspond to citrus and vegetables farming (476.22 and 457.81 respectively). Higher values of this index were observed by Errecalde et al. (1991) for similar soils (an average value of 403 for marshy soils with rice farming, and 180 for soils with vegetables crops).

Generally, the extractable fraction is present in a low proportion in alkaline soils. Andersson (1975) and Lake et al. (1984) observed that the extractable form of metals represents the 10% or less of the total content. For Cd, the extractable fraction could reach the 18% of its total content in soils (Andersson, 1975). In the studied area, higher values of Extractable/total ratio for Cd, Cu and Pb can be observed in zones 3 and 4 (36.14, 29.91 and 22.28% respectively), whereas Co and Zn reach its maximum values on citrus and vegetable crop zones. Zone 8 present the higher values for Cr. The lower values correspond to the dunes cordon (zone 5). The sequence of values distribution for this index is: Cd > Cu > Pb > Zn > Ni > Co > Cr.

Making a global evaluation of the results obtained, it can be observed that the higher values, as on the indexes as on the total content and the extractable fraction of the seven metals studied, are centered in the marshy zones. Mainly, in the north zones except the Zn/Cd ratio that is higher on the south of the marsh (zone 2).

These results are coincidents with the geographical distribution of the urban and industrial centers in the area. These are located, mainly, in the north-northeastern part of it. This situation suggests dumping of waste water and industrial residues directly on zones 3 and 4, including on zone 2.

Considering all the studied parameters, a clear incidence of human actions toward the pollution of this area can be observed. The zones with smaller values of the indexes, although they overcomes in some cases the maximum values of these, are the zones of citrus and vegetable crops. Furthermore, this zones presents high level on Cd and Co too, which could be due to the undiscriminating use of fertilizers and pesticides for farming maintenance.

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