

ELEMENT DISTRIBUTION OF SOME SOILS OF CONTINENTAL CHILE AND THE ANTARCTIC PENINSULA. PROJECTION TO ATMOSPHERIC POLLUTION.

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Abstract. The elemental content of some soils of continental Chile and the Antarctic Peninsula are reported. The elements: Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb were analyzed. Trace elements differed among soils. The values for Cd are greater than those reported elsewhere. The organic matter content was observed to have a great importance in the Antarctic Peninsula soils. Differences between local element contents and the mean concentrations values for the terrestrial crust were found. In order to get a better determination of the origin of the aerosol the enrichment factor, used as a criterion to establish the origin of the trace elements in the atmospheric aerosols, should be recalculated based on the local soil.

1. Introduction

The study of the atmospheric aerosol is essential when technical decisions about pollution problems are necessary. The chemical nature, the mass-size distribution and the origins of the aerosol are very important.

The soil particles blown by the wind are one of the sources contributing to the airborne particulate matter. These particles can remain suspended in the air according to their sizes, shapes and chemical composition. Also they can be transported for long distances.

The atmospheric aerosol contains trace elements which can be used to establish its origins. In this sense, several methods are known; one of them, the criterion of the enrichment factor (EF) is easy to use as a first approximation (Duce *et al.*, 1975). This criterion introduces the mean element concentrations of the terrestrial crust. The EF is usually calculated using Mason's international mean values of samples taken within a depth of several kilometers (Rahn, 1976; Mason, 1966). that it allows an international comparison of the results obtained (Rahn, 1976). But pollution problems are mostly local problems; thus, in order to obtain a more precise determination for the origin of the elements in a given site, the element contents of the local soils should be known (Préndez and Carrasco, 1982; Préndez *et al.*, 1983, 1985).

The variety of soils existing in Chile requires the analysis of soils from different regions of the country (Atlas de Chile, 1987). Therefore, the purpose of this work is to determine the element contents in soils from the Northern, Central and Southern parts of continental Chile and from the Antarctic Peninsula, in order to calculate the real EF.

2. Materials and Methods

Chile is located at the south west of South America between 17° 30' and 90° S lat. The continental part is located between 66° 30' and 75° 45' W long.; the Antarctic sector is situated between 53° and 90° W long. Integrating the Chilean territory are also some islands in the Pacific Ocean. The mean width of the country is about 177 km; the maximum width is about 380 km at 27° 7' S lat. The relief of the country is undulate and mountainous; no more than 20% of the surface is flat; it presents three morphological characteristics: the Andes range, the Coast range and the Central Valley between them. All samples were taken in four different regions of the Central Valley.

Thirteen surface soil samples (0 to 7 cm) along continental Chile and fifteen samples from two of the South Shetlands Islands at the Antarctic Peninsula (King George Island and Doumer Island) were taken. Samples were air-dried and screened through a 2-mm sieve and then crushed to pass through a 0.1-mm sieve (140 mesh). Some characteristics of the samples are given in Table I.

Table I. Some characteristics of the soil samples.

Site	Geographical location	pH	Organic matter (%)
IVth R.	29° 10' - 32° 5' S lat.	6.8 - 0.2	1.78-0.22
M. R.	32° 55' - 33° 40' S lat.	ND#	0.69-0.08
VIth R.	33° 5' - 34° 50' S lat.	6.3 - 0.8	3.67-3.00
Xth R.	39° 20' - 43° 40' S lat.	5.8 - 0.0	22.6 -6.40
K.G.I.#	62° 11' lat.S, 58° 55' W long.	7.5 - 0.6	0.91-0.27
D.I.æ	64° 52' lat.S, 63° 36' W long.	5.3 - 0.5	13.8 -9.20

#: not determined

æ : Doumer Island

: King George Island

The soils are classified as Entisol and Aridisol in the IVth Region, Mollisol and Inceptisol in the Metropolitan Region (M. Region), Inceptisol and Entisol in the VIth Region, and Inceptisol in the Xth Region. The soils of the Antarctic Peninsula are not classified. The pH was measured in a 1:2 soil/water ratio and the organic matter was determined by the Walkley-Black procedure (Page *et al.*, 1982).

For the sample dissolution different methods by wet digestion were tested (Bernas, 1968; Langmyhr and Paus, 1968; Page *et al.*, 1982).

The use of the Parr-teflon bomb failed with the samples analyzed due to their incomplete dissolution, and the persistence of some organic matter (OM) which precipitated after the dissolution process.

The method recommended by Carrasco and Préndez (1984) using a platinum crucible was utilized but the use of 100 mL teflon beakers was preferred because they are more easily handled and allow seeing the completion of OM decomposition. A modification consisting in a previous digestion with HNO_3 and HClO_4 was introduced to destroy the OM (each 0.5-g sample was digested on a hot plate with 3 mL of HNO_3 and 1 mL of HClO_4 at 120 to 140°C for 1 hr and then the mixture was evaporated until fumes of HClO_4 appeared). This was applied to all samples in order to avoid differences in the matrix of the final solution.

The analyses were run twice and the reported average values are expressed on soil dry basis at 105° C; the elements Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb were quantified by flame atomic absorption using a Perkin Elmer Model 460 Atomic Absorption Spectrophotometer.

Standard solutions containing all the elements in concentrations equivalent to those of the samples and blanks were subjected to the same acid treatments as the samples. Then the efficiency factors and the concentration of the blanks were calculated to correct all the measured concentrations. The concentrations of the blanks were different from zero only in the case of Al, Cu, and Pb.

3. Results and discussion

The total content of some chemical elements in soils of the different regions from continental Chile, are given in Table II. The results show that metal content depends upon the region studied. Within each region the coefficients of variation were high for some elements and low for others. These variations are associated with the different origins of the soils: marine terraces, alluvial sediments, and vicinity of a copper mine.

The high variability observed in the M. Region for Pb could be associated to some contamination from the air. The high Cu and Mn VIth Region are associated with an area close to one of the main copper mines of Chile (El Teniente). The high Al concentration found in soils from the Xth Region is attributed to the presence of abundant amorphous Al silicates that dominate their clay fraction.

The mean concentrations obtained in this work and those reported by Schirado *et al.* (1986) for a non-polluted soil and for a soil polluted by waste-municipal water in the M. Region, are given in Table III.

The contents of Mn, Cu, and Zn obtained in this study are similar to those of a no-polluted soil; the Cr and Ni contents are between the values given by Schirado *et al.* (1986); the Cd content obtained in this work was higher than the value given for the polluted soil.

Table II. Range, arithmetic means (X) and coefficients of variation (CV) for total content of some chemical elements in soils of continental Chile.

Elem.	IVth R. ‡		M. R. ‡‡		Vth R. ‡‡		Xth R.	
	Range X	CV, % n# = 3	Range X	CV, % n = 4	Range X	CV, % n = 4	Range X	CV, % n = 2
Major elements (%)								
Al	7.41-7.59 7.50	1	ND## --		ND --		9.86-11.17 10.5	6
Fe	3.75-4.08 3.89	4	3.39-4.44 3.99	10	7.30-8.72 7.58	7	4.9	0
Trace elements (mg kg⁻¹)								
Cr	78-89 82	6	31-54 40	20	23-43 36	21	73-91 82	11
Mn	997-1446 1153	18	837-925 890	4	1114-3006 1662	47	404-1556 980	59
Co	33-44 39	12	ND --		ND --		12-25 19	4
Ni	13-26 18	31	43-47 44	4	43-48 45	5	11.4-22.9 17	33
Cu	77-116 92	19	78-129 106	20	168-655 328	59	108-140 124	13
Zn	73-93 84	10	143-185 154	12	148-239 178	20	86-197 142	39
Cd	2.7-3.3 3	8	5.1-5.1 5	10	5.2-6.3 6	10	UDL‡ --	
Pb	(17-(30 (23	7	(32-143 68	62	95-201 127	34	UDL --	

‡ R. : Region

‡‡ From Carrasco and Préndez, 1984

n : number of samples

ND : not determined

‡ UDL : Under detection limits (0.025 mg kg⁻¹ for Cd, and 0.50 mg kg⁻¹ for Pb).

Table III. Mean concentrations of soils of the Metropolitan region given by different authors.

Elem.	Poll. soil‡	Non-poll. soil‡	This work
Cr	73	6.6	40
Mn	1574	868	890
Ni	66	19	44
Cu	653	112	106
Zn	328	112	154
Cd	3.8	ND#	5

‡ From Schirado *et al.*, 1986.

ND : not determined

In the Antarctic Peninsula, the metal contents obtained for King George and Doumer Islands are given in Table IV and showed large differences between the islands. The data obtained for Doumer Island showed a clear relation with the OM content of the soils depending on whether, the OM content was less or greater than 12%. The soils with more than 12% showed lower contents of Al, Fe, Cr, Ni than soils with OM content lower than 12%; the Co content was about four times lower. The Cu and Zn contents were about four times the levels obtained for the soils with less than 12% of OM.

The high OM content of some soils is attributed to the presence of penguins which deposit their excreta on the surface soil. The high Cu and Zn concentrations found in these soils could be related to this process but analyses of the penguins excreta should be made to confirm this hypothesis.

The Cd contents obtained in this work for the different Chilean soils (Continental Chile and Antarctic Peninsula) are higher than those reported by Page *et al.* (1989) and by Ferguson, (1990). However, these to some analytical problems because the procedure used was properly checked by using blanks and standard solutions.

The Cd contents obtained for the soils of Continental Chile (2.7 to 6.3 $\mu\text{g kg}^{-1}$) correspond to soils that have not been exposed to any evident source of contamination. Therefore, the Cd contents would be attributed to the parent material as Fergusson (1990) has assumed for soils uncontaminated, having less than 0.1 to 11 $\mu\text{g kg}^{-1}$ of Cd.

In the Antarctic Peninsula the values found (3.8 to 9.2 $\mu\text{g kg}^{-1}$ Cd) were also higher than those reported by the literature. Also, in the Doumer Island a direct relation between the Cd content and the OM content, was observed. Fergusson (1990) has reported a similar relation for some soils derived from shales of California.

In order to see how the local element concentrations may affect the enrichment factors, the total mean values for continental Chile, the Antarctic Peninsula and the terrestrial crust are compared. The values are shown in Table V. Data obtained for soils sampled under the forest in Torres del Paine, a biosphere reserve, located at the

Table IV. Range, mean arithmetic values (X) and coefficients of variation (CV) for total content of some chemical elements in the soils of two islands of the Antarctic Peninsula.

Elem.	King George Island		Doumer Island			
	X	CV, %	OM < 12 %		OM > 12 %	
	n=6		X	CV, %	X	CV, %
			n=4		n=5	
Major elements (%)						
Al	ND#		7.02-8.03		1.15-5.04	
			7.54	5	2.56	58
Fe	3.39-6.51		3.39-5.11		0.87-2.83	
	5.54	19	4.03	18	1.47	51
Trace elements (µg kg ⁻¹)						
Cr	17-54		63-86		25-53	
	30	35	71	15	33	31
Mn	1138-1671		644-914		329-865	
	1201	13	771	16	575	33
Co	ND	--	7.8-28		1.2-7.3	
			19	45	4.7	46
Ni	38-47		12-22		2.9-18	
	44	8	15	31	9.8	53
Cu	79-167		63-148		190-570	
	129	26	111	35	428	32
Zn	40-97		152-211		127-1301	
	81	25	187	28	809	72
Cd	3.8-7.1		2.8-5.1		1.0-8.0	
	5.6	21	3.5	18	5.2	47
Pb	38-82		14-45		20-(34	
	58	17	32	36	26	21

n : number of samples

ND : not determined

XIIth Region are also given (Covarrubias and Préndez, 1990, personal communication). Torres del Paine is a natural reservation located at a very inaccessible area in the Andes range and is a non-polluted place.

Table V shows that all the elements analyzed in this work except

Mn are higher than those found for Torres del Paine. The low contents of Cu, Zn, and Cd of the soils from Torres del Paine could indicate a different soil origin than those of the other regions of the country, and also support the hypothesis of an animal contribution to the soils of Doumer Island. For continental Chile Cr and Ni are lower, Al, Fe, Mn, and Co are similar, and Cu and Zn are higher than the values reported for the terrestrial crust. For the Antarctic Peninsula Al, Fe, Cr, Co, and Ni are lower, Mn is similar and Cu, Zn, and Cd are higher than those reported for the terrestrial crust.

Table V. Arithmetic means of total element concentrations (X) for some chemical elements in soils from Chile and for the terrestrial crust.

Elem.	Continental Chile X	Antarctic Peninsula X	Torres del Paine [‡] X	Terrest. Crust [#] X
Major elements (%)				
Al	9.00	4.83	0.40	8.2
Fe	5.09	2.61	0.43	5.6
Trace elements (mg kg ⁻¹)				
Cr	60.0	49.5	2.5	100
Mn	1171	662	3006	950
Co	28.7	11.1	2.3	25
Ni	31.1	12.1	2.4	75
Cu	163	287	56	55
Zn	140	532	58	70
Cd	4.6	7.5	0.4	0.2
Pb	72.6	UDL [‡]	7.1	12.5

[‡] From Covarrubias and Préndez, 1990, personal communication.

[#] From Mason, 1966.

[‡] UDL : Under detection limits (0.50 mg kg⁻¹).

The enrichment factors (EF) are calculated by the following formula:

$$EF = \frac{C_i \text{ aerosol} / C_{ref. \text{ aerosol}}}{C_i \text{ crust} / C_{ref. \text{ crust}}}$$

where C_i and C_{ref} correspond to the concentrations of the element i and the element of reference used, respectively.

The origin of the elements in the aerosol, natural or anthropogenic, is determined by the value of EF (equal or greater than 1). Therefore, if in the formula for EF the elemental concentrations given for the terrestrial crust are changed for those determined for the local soils, it is possible to observe some differences in the values of the EF; in this way the use of the real content of the elements of the area sampled, i.e., the element concentrations of the local soils can give some differences in the assignment of the origin of the elements in the aerosol.

In Table VI some examples of the EF values based on the terrestrial crust and the local soils are shown. The values were taken from published data (Carrasco and Préndez, 1984; Del Carpio, 1987; Préndez *et al.*, 1989) where these ideas about EF had also been presented. Examples for the IVth and Xth regions are not given because their aerosols have not been analyzed yet.

Table VI. Mean EF based on the terrestrial crust (T.C.) and the local soil (L.S.) for different regions of Chile.

Elem.	EF values					
	M. Region [‡]		VIth Region [#]		K.G.I. [*]	
	T.C.	L.S.	T.C.	L.S.	T.C.	L.S.
Ni	49	62	4.1	1.6	30	39
Cu	862	482	5.7	14.7	161	70
Zn	2665	104	8.1	11.4	261	226

[‡] From Del Carpio, 1987.

[#] From Carrasco and Préndez, 1984.

^{*} From Préndez *et al.*, 1989.

Depending on the site sampled the values of EF can be dramatically different, as in the case of Zn in the M. Region. However these changes do not always reflect a different origin of the aerosol. Even if EF values greater than 1 point to an anthropogenic origin no certain limit exists and values of 6 to 10 are generally considered to be the limiting ones and some special situations can occur. For instance:

a) In the VI Region where a very great copper-mine complex is located, including extraction, refining and so on, the origin of Cu in the aerosol should be changed from natural to anthropogenic. It can also be established that the anthropogenic source is undoubtedly the copper-mine El Teniente.

b) In the Doumer Island (Antarctic Peninsula) the EF values reported by Préndez *et al.* (1989) were calculated based on the elemental concentrations of soils of King George Island, because at that time the values of the elemental concentrations of soils of Doumer were not available. As it can be seen from the data reported in this

paper, the values of Doumer are, in general, different from those of King George Island (see Table IV). The OM content is a very important factor to be considered. If the EF values are calculated again based on the elemental content of the soils of Doumer Island with different OM content, some changes can be observed which are shown in Table VII for the elements Ni, Cu, and Zn.

Table VII. Arithmetic means of the EF for Ni, Cu and Zn in atmospheric aerosols of Doumer Island (Antarctic Peninsula) according to the references used.

Elem.	T.C.	K.G.I. Soil	Doumer Soil	
			(<12% OM)	(>12% OM)
Ni	21	35	75	42
Cu	333	145	123	12
Zn	904	783	247	21

Table VII shows some drastic changes of the EF values. For Ni and Zn the origin is confirmed as anthropogenic. For Cu the changes seem to lead to a natural origin specially when soils with a high OM content are considered.

4. Conclusions

The data presented in this work show that the element concentrations in soils are very different within the country.

In the Antarctic Peninsula the concentrations differ from one island to another. In some areas the elemental composition of the soil is closely related to the OM content.

When the EF are calculated based on the element concentrations of local soils instead of the values of the terrestrial crust, the assignment of the origin of the elements in the atmospheric aerosol in general remain the same, but in some special cases this assignment should be changed.

If the EF are used to determine the origin of elements in the atmospheric aerosol in a particular region and the concentration of certain elements in the local soil are very different from concentrations reported in published references, local pollution may be suspected. Then the EF values should be recalculated, based on concentrations found by sampling the local soils, in order to determine the origin of the element of concern in the atmospheric aerosol.

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