

Heavy metal contamination in some soils of the McMurdo Sound region, Antarctica

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Abstract: Soil samples from eight sites at Marble Point and Pram Point, McMurdo Sound region, contaminated by human activities were examined for heavy metal content, using sequential extraction methods. The redistribution of lead, zinc and copper arising from point sources of these metals was demonstrated. The levels found are not considered to represent serious pollution but do indicate that human activities can change the chemistry of the Antarctic environment in localized areas.

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Introduction

Antarctic ecosystems are probably the simplest of any in the world because of the exceedingly cold climate, the absence of precipitation and significant vegetation, and the very slow rate at which soil weathering takes place. After almost four decades of intensive scientific activity in the McMurdo Sound region of Antarctica, there is now an increasing awareness of the potential impact of human activities on the Antarctic ecosystems. However, while the soils have been widely studied, there are few quantitative data available to provide measures of either the rate at which natural processes occur, or the extent to which disturbance of the ecosystem by human activities may have taken place.

In 1990, while carrying out studies of soil moisture in the active zone and permafrost at Marble Point, debris from a construction camp in use in 1958/59 was observed scattered about the soil surface at the old camp site. This included metallic substances as well as organic debris of various kinds. At some sites, where material had been piled up and burnt, ashes, nails, metal scraps and other debris were present.

Because some of the metal items at the soil surface, particularly copper, were strongly oxidized, the soils at several sites were sampled to determine the extent to which metal contamination may have leached into the soil. For comparative purposes, a soil from a site close to the construction campsite that showed no obvious signs of disturbance was also sampled. In addition samples were also collected at Scott Base, on Ross Island, from a site where an old building had recently been removed. The results of the analyses of these samples are reported here.

Materials and methods

Description of soils and the soil environment

The soils at Marble Point and Scott Base are typical of Antarctic soils found on tills on relatively young (<15000 years) glacial

retreat surfaces (Campbell & Claridge 1987). They consist of bouldery sands with the <2mm fraction (excluding boulders and cobbles) around 50% and with silt and clay fractions commonly <4% of the 2 mm fraction. The soils are unweathered, loose, and, because of the absence of plant cover, contain negligible amounts of organic matter. They are underlain by hard, ice-cemented permafrost at depths of between 35 and 60 cm. At Marble Point, the soils are alkaline, with pHs between 8.0 and 9.5. They commonly contain 1–2% by weight of water-soluble salts, largely sodium chloride and sulphate, although smaller proportions of other ions are also present. At Pram Point, the salt contents are generally somewhat lower. Undisturbed soils have moisture contents ranging from 0.5% at the surface to 6–10% at the permafrost table. Within the permafrost, the frozen soil material is generally completely saturated with ice or even contain excess ice, although close to the surface of the permafrost there may be some pore space not completely filled with ice (Campbell *et al.* 1994).

The soils from Marble Point and Scott Base are formed in an environment which is moist, relative to most of Antarctica. Mean annual temperatures are about –18°C, although summer temperatures may rise to +10°C or more (Sansom 1984), and the soils are occasionally moistened near the surface by summer snowfalls.

Soil sampling

The artefacts at Marble Point are believed to date from 1958/59 when a construction camp was established as a base for engineering investigations to assess the suitability of the area for a land-based runway. Following the abandonment of the project in 1959, some clean-up of the site took place and the buildings were subsequently demolished and removed. Remaining material was crushed and partially buried by bulldozing during or subsequent to the tidy-up. The artefacts studied had been in

position since that time.

At Marble Point, soil samples were collected in 1990 from directly beneath, at the edge of and 30 cm away from a crushed lead battery; from directly beneath a coil of wire, from beneath an accumulation of rusting cans, and from an adjacent site where no cans were present; from directly beneath the site of a rubbish fire; and from an apparently undisturbed site some 50 m from the battery site in an area where no artefacts were obviously present. The "undisturbed" site would doubtless have been walked over many times during the period of occupation of the camp. Details of the sample sites, including site numbers and sampling depths are given in Table I.

At Scott Base a site was sampled by the door of the former mess hut, which had been removed the previous season. Although no artefacts were seen, apart from a scatter of fine debris, kitchen rubbish was stored close by during the 25 years the building was in use and the site would have been subjected to continuous contamination from human activities during this time.

Table I. Sample depths and results of preliminary acetic acid extraction of samples. Element concentrations as $\mu\text{g g}^{-1}$ soil. nd = not detected.

sample	depth (cm)	Pb	Zn	Cu
Marble Point, beneath crushed lead battery				
578b	20–30	28.5	0.36	0.04
578c	30–40	0.25	0.04	<0.04
578d	40–55	<0.09	0.03	<0.04
578e	>55	1.8	0.008	<0.04
Marble Point, edge of battery				
643a	0–5	11.6	0.61	0.05
643b	10–15	0.09	0.07	<0.03
643c	20–30	0.33	0.03	<0.03
Marble Point, 30cm from battery				
643d	0–5	3.7	0.24	<0.04
643e	10–15	1.02	0.17	<0.04
643f	20–30	0.75	0.05	0.19
Marble Point, beneath copper wire on surface				
579a	0–2	nd	3.3	10.6
79b	2–5	nd	1.6	0.18
Marble Point, rubbish dump sites under rusty cans				
580a	0–2	<0.09	4.0	0.11
adjacent to 580a but no cans present				
580b	0–5	<0.09	4.9	0.04
Marble Point, site of fire				
582b	0–3	0.46	488	3.6
582c	3–10	<0.04	0.03	<0.04
582d	10–16	<0.09	1.30	<0.04
Scott Base, old mess hut site, by door				
601a	0–1	<0.09	8	0.24
601b	1–8	0.2	62	1.7
601c	8–19	0.64	10.6	1.3
601d	19–29	<0.09	0.42	0.10

Sample collection and preparation

Pits were excavated to the level of the ice-cement; samples were collected from the side of each pit using a clean trowel and stored in plastic bags. Samples were collected from the bottom of the pit upwards to avoid possible contamination from surface material falling down the sides of the pit. When returned to the laboratory, they were air-dried at 30°C and sieved through a 1 mm nylon mesh in a clean area. All subsequent analyses were on the <1mm fraction and were carried out in a class 100 clean room. Microscopic examination ($\times 50$) did not reveal any particulate material (PbO_2 , CuCO_3 , ZnO) which could be ascribed to the point sources. However, the possibility that particulate matter contributed to the analyses remains.

Metal extraction

Sodium acetate was Aristar quality. Ammonia solution and acetic acid were purified by isopiestic distillation of the Analar (BDH) reagents. Sodium pyrophosphate (Analar) was purified by electrolysis using a mercury pool cathode. Mercury used for electrolysis was BDH Aristar grade.

To obtain a preliminary estimate of the presence of heavy metals 1g portions of each sample were extracted with 4 ml 0.1M acetic acid and centrifuged at 3000 rpm in a centrifuge of 100 mm radius.

The sequential extractions were designed to identify the forms in which the heavy metals are found in the soils by using extracting reagents which preferentially attack different sites. The methods used are applicable to soils with contents of clay minerals or organic matter typical of soils in temperate regions, which can absorb or complex metal ions. Antarctic soils have low clay contents, generally around 1–5%, and extremely low organic matter contents. A four step extraction system was used. 1 g portions were extracted for one hour with 8 ml of 1.0M ammonium acetate adjusted to pH 7, centrifuged, and the supernatant removed. This procedure extracts water-soluble ions and those on the exchange complex of clays and organic matter (Chapman 1965). The residue was then extracted with 8 ml of sodium acetate at pH 5 for 2 h, with intermittent agitation, centrifuged and the supernatant removed for analysis. This procedure removes metal ions bound to carbonates as well as other acid-soluble cations (Tessier *et al.* 1979). The residue from this step was then extracted with 8 ml of 0.04M hydroxylamine hydrochloride in 0.5M acetic acid for 6 h at 90°C to extract metal cations bound to iron and manganese oxides (Tessier *et al.* 1979). The final extraction was made with 10 ml of sodium pyrophosphate for 12 h to render organic matter and the associated metals soluble (Elsokkary & Låg 1978). Residues were not resuspended and washed between sequential extractions, but the maximum carryover of extractant in consecutive steps was measured as 5%.

Analysis

In all extracts, the heavy metals Pb, Zn, Cu and Cd were determined using differential pulse anodic stripping voltammetry (DPASV) and, for Cu and Zn, electrothermal atomic absorption spectrometry (ETAAS).

For DPASV, a PAR 384B Polarographic Analyser and PAR 303A hanging mercury drop electrode was used. Instrumental parameters were: drop size, medium; N₂ purge, 10 min; stir, fast; deposition time, 5–10 min; pulse height, 25 mV; scan rate 5 mV s⁻¹. Typical measurements involved addition of 50 µl (upper horizon)–3000 µl (lower horizon) of extract into 10 ml Milli-Q water and 500 µl 1M KNO₃ (Aristar) in the cell. Calibration was by spiking with standard solutions of analyte metals. All measurements were relative to a blank (instrument subtracted) prepared using the same aliquot of pure extractant and KNO₃. Typical blanks were: for hydroxylamine, 0.4 ppb Cu, 0.03 ppb Pb, 3 ppb Zn; for Na₄P₂O₇, 0.05 ppb Cu, 0.03 ppb Pb; for acetate buffer, 2 ppb Cu, 4 ppb Pb, 0.8 ppb Zn. Extracted humic matter was problematic only for pyrophosphate extracts, and particularly for Cu and Zn whose stripping peaks were most affected by humate tensammetric waves. Cu and Zn in these extracts were determined by ETAAS.

A GBC 2000 series furnace and controller and a GBC 903 spectrometer with PAL 1000 autosampler was used for ETAAS. Resonance lines used were 324.7 nm (Cu) and 213.9 nm (Zn); continuum source background correction was used routinely. Standards (0.01–0.06 ppm Cu, 0.004–0.035 ppm Zn) were prepared in the appropriate extract. Sample injections were Cu: 12 µl of extract (diluted 2–100 fold with extractant) + 12 µl 1% HNO₃ modifier; Zn: 5 µl (diluted 40–2000 fold) + 5 µl 1% HNO₃ (for NH₂OH extracts). Furnace conditions were: dry 110°C (ramp 30s, hold 5s), 140°C (20, 5); ash 650°C (15, 5); atomize 2400°C (1.0, 2.0); clean 2500°C (1.0, 1.0).

The results obtained by the two methods were in satisfactory agreement. For Cu the values were typically within ± 10–20% by the two techniques; for Zn the ETAAS values were typically 20–40% (average 25%) higher, perhaps indicating incomplete separation of colloidal material during centrifugation. By ETAAS the lower limit of measurement (5 × DL) was c. 0.001 µg g⁻¹ for Cu and Zn. By ASV the lower limit was set empirically by the concentration of analyte, diluted 20-fold, which gave a stripping current of 5nA after 10 min deposition. For Cu, Pb and Zn this was 0.04, 0.09 and 0.03 µg g⁻¹ respectively. For the wide range of analyte concentrations all DPASV RSDs were in the range 0.4–5%. Humified organic matter was measured by the absorption of the pyrophosphate extract at 465 nm, using fulvic acid solutions as standards. For more complete analytical details see Amin (1993).

Results

Preliminary extractions

Levels of zinc, lead and copper (Table I) were barely detectable in the extracts from the reference sites, but could be found in the

samples from contaminated sites. Cadmium levels were below the detection limits at all sites (also for sequential extractions). A relatively large amount of lead, and smaller amounts of zinc, were detected under the battery and at the edge of the battery, while smaller but significant amounts were found 30 cm laterally. The concentration falls off in the horizon beneath the surface but increases again slightly at the permafrost level. Copper levels are low in the extracts but seem to follow the same trend.

This indicates that lead, zinc and possibly copper are released from the lead battery, and are present in particulate or absorbed form immediately beneath. Lead and zinc have moved laterally, presumably by wind or water, at least 30 cm. Lead and zinc have also moved vertically downwards.

Sequential extractions

Organic matter estimated by measuring the absorption at 460 nm of pyrophosphate extracts of these soils, gave extremely low values of between 0.003 and 0.016%. The highest value found was 0.016%, in sample 580a, collected amongst rusting cans, where some residual traces of organic matter might be expected. Similarly the soil at Scott Base (601a), subject to long-term contamination with organic matter (kitchen refuse, slops, etc.), also contained 0.015% carbon. Although these values are five times that of the reference site, they may be considered negligible. In general extractable metals were found predominantly associated with the oxide and carbonate phases. With the exception of site 579, exchangeable metal represented a minor fraction (<10%) of total extractable metal. This is consistent with the low organic content and low CEC of these poorly weathered soils. The maximum copper binding capacity for soil humic acids (HA) has been reported as 1.2 × 10⁻³ mol (gHA)⁻¹ (Powell & Town 1993). Assuming 50% C in soil humic acid this binding capacity is equivalent to 24 µg g⁻¹ in a soil with 0.016% C.

The sequential extractions which used somewhat more powerful extractants, yielded higher amounts of lead and zinc, particularly in the oxide form and (for Cu) the organic forms at the reference site (Table II). There may be some slight contamination, derived from the burning of vehicle or heating fuels.

The sequential extractions of the lead battery site (Table III) showed that the bulk of the lead is associated with the oxide form or carbonates. Lead was originally present in the battery either as metallic lead or lead oxides in the plates, or as lead sulphate or lead ions associated with the electrolyte. The lead in the surface sample immediately below the battery could have fallen from the plate remnants as oxide. This has moved a little way down the profile and laterally, probably still in the particulate form. Lead in the ionic form has reacted with carbonate ions to precipitate as lead carbonate or perhaps the more stable hydroxy carbonate (white lead). This could account for the high concentrations of lead in both the oxide and the carbonate form at the permafrost surface. Some lead appears in the “organic”

Table II. Results of acetic acid and sequential extractions of the reference site samples. Reference site situated 50 m N of site 578. Values in $\mu\text{g g}^{-1}$.

sample	depth cm	acetic acid	sequential extractions				
			exchg.	carbonate	oxide	organic	
Pb	645b	0-5	<0.01	<0.09	<0.09	0.14	<0.09
	645c	5-20	<0.01	<0.09	<0.09	0.14	0.12
	645d	20-30	<0.01	<0.09	<0.09	0.14	<0.09
Zn	645b	0-5	0.11	<0.03	0.4	1.4	<0.28
	645c	5-20	0.15	<0.03	0.7	1.0	<0.28
	645d	20-30	0.02	0.04	0.09	1.4	<0.28
Cu	645b	0-5	0.02	<0.04	0.08	0.1	0.53
	645c	5-20	<0.01	<0.01	0.08	0.15	0.64
	645d	20-30	<0.01	0.11	0.21	0.48	0.74

fraction although, given the minimal amount of organic matter present and its finite metal binding capacity, this is likely to include lead in the oxide form that had not been dissolved during the preceding extractions.

Most of the zinc appears in the oxide fraction, but appreciable amounts also appear in the pyrophosphate extract. Zinc oxide is less stable than lead oxide. Surprisingly, little zinc is associated with carbonate. The zinc in the pyrophosphate extract may be associated with organic matter, but, as with lead, it may represent residual oxide not previously extracted. As the battery plates were not analysed, it is not known whether the zinc is associated with lead in the battery, or was external, associated with terminal clamps, copper wiring, etc. Copper is also found in the soil associated with the lead battery, (probably derived from wiring) but only in very small amounts, mainly as the carbonate.

More can be learned about the behaviour of copper from its occurrence under a coil of copper wire (Table IV). Copper and zinc were found at high concentration in the acetic acid extract of soils from immediately below the copper wire (Table II), and were detected in material 5 cm down. Samples were not taken from deeper layers, and therefore the extent of movement can not be judged.

The sequential analyses (Table IV) show that under the copper wire, copper is present largely in the ionic form or as carbonate, with a smaller proportion as oxide. Only a small proportion of the copper has penetrated more than 2 cm into the soil. This is probably because the copper metal, has, in the first instance, to be oxidized and dissolved in what little moisture is present. It may then react with carbonate or hydroxide ions present to precipitate as copper carbonate or oxides, probably through the basic sulphates or basic carbonates ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$, $\text{CuCO}_3 \cdot 3\text{Cu}(\text{OH})_2$). At an adjacent site copper pipe was observed to be corroding, with the liberation of green copper salts on the surface of the soil. However insufficient material was available to identify these phases.

Zinc was found associated with the copper, although its origin was not obvious. It was, however, more mobile, moving further into the soil indicating greater solubility of Zn

Table III. Results of analyses of sequential extracts from three sites associated with a crushed lead battery at Marble Point. Results expressed as $\mu\text{g g}^{-1}$ soil (particle size <1mm).

sample	depth cm	exchg.	carbonate	oxide	organic
Pb beneath centre of crushed lead battery					
578a	20-30	75	492	460	99
578b	30-40	6.3	50	126	74
578c	40-55	1.0	13	23	14
578d	<55	1.4	116	187	33
beneath edge of battery					
643a	0-5	89	287	431	242
643b	10-15	0.08	0.29	0.33	10
643c	20-30	3.8	47	112	10
30 cm from edge of battery					
643d	0-5	18	40	97	51
643e	10-15	2.3	28	244	15
643f	20-30	3.9	28	68	25
Zn beneath centre of crushed lead battery					
578a	20-30	0.16	0.22	15	2.7
578b	30-40	0.05	0.10	5.3	0.47
578c	40-55	<0.03	0.07	1.6	0.20
578d	<55	<0.04	0.07	1.1	<0.03
beneath edge of battery					
643a	0-5	0.37	1.1	4.2	1.0
643b	10-15	0.05	0.08	1.6	0.4
643c	20-30	<0.03	0.25	1.6	<0.03
30 cm from edge of battery					
643d	0-5	<0.03	0.56	6.5	1.7
643e	10-15	0.03	0.39	6.6	1.9
643f	20-30	<0.03	0.40	2.0	0.2
Cu beneath centre of crushed lead battery					
578a	20-30	<0.04	0.18	0.34	0.71
578b	30-40	<0.04	0.21	0.30	0.88
578c	40-55	<0.04	0.24	0.10	0.81
578d	<55	<0.04	0.20	0.37	1.1
beneath edge of battery					
643a	0-5	0.19	1.81	<0.04	<0.2
643b	10-15	<0.04	0.11	0.08	<0.2
643c	20-30	<0.04	0.84	<0.04	0.9
30 cm from edge of battery					
643d	0-5	0.18	0.29	<0.04	0.4
643e	10-15	<0.04	0.08	<0.04	0.6
643f	20-30	<0.04	0.05	<0.04	1.0

in the alkaline soil.

Under the soils contaminated by rusting cans (580), zinc levels are high, while traces of copper and lead are also present. Zinc may be present in the solder in the cans or be associated with the tinplate, although other sources of zinc, such as zinc-coated steel may also be present in the dump. At the fire site (582), levels of zinc are extremely high at the surface. It is probable that zinc-coated steel was associated with the wood (nails, bolts, wire, etc.), contributing zinc to the ash. Tin was not looked for in this study but would be expected under the rusting cans.

The sequential extractions show that at the fire site (582,

Table IV. Results of sequential extraction of Cu and Zn from soils associated with copper wire, Marble Point ($\mu\text{g g}^{-1}$).

		exchangeable	carbonate	oxide	organic
Zn	579a	1.5	1.5	2.7	1.9
	579b	5.8	6.4	11.0	8.4
Cu	579a	35	37	13	12
	579b	1.7	2.1	1.8	3.8

Table V) zinc is present largely as the oxide, but, as a consequence of its reactivity, is also present in the ionic form, as carbonate, and in the humic fraction. The high levels of zinc in the latter fraction are more likely to result from extraction of zinc not completely released by the preceding extraction, rather than be associated with organic matter. The highest amount of lead extracted is found in the organic fraction; this may well be associated with organic matter, although pyrophosphate only extracted 0.01% organic carbon, about three times the amount found in the reference site. Copper is found largely in the carbonate and organic fractions.

The one site from Scott Base (601), (Table V) on rock of totally different composition from the reference site, also shows high levels of zinc, and appreciable amounts of lead and copper, which extend at least 20 cm down the profile. Zinc and lead are present largely as carbonate and oxide, with lesser amounts in the organic fraction, while copper appears largely in the organic fraction.

The origin of these heavy metals is not immediately apparent, but possible sources are leaching of zinc oxides from metal surfaces such as guy wires, garbage tins or wire mesh, lead from painted surfaces, tin cans etc., and copper from wire scraps. The buildings themselves were clad with aluminium sheet, but the passages between buildings were constructed from galvanized sheet steel (Quartermain 1971). It is evident that even without obvious contamination, human activity adds heavy metals to the environment.

Discussion

Lead

The reference site at Marble Point contains very low levels of lead, mostly as oxide. This may represent naturally occurring levels, as it is evenly distributed down the profile, but could be due to the burning of lead-containing fuels during the period of occupation of the camp. Lead levels are significantly higher in the contaminated site at Scott Base than in the reference site at Marble Point. It is possible that these levels could also arise from the burning of lead-containing fuel, but this would need to be checked by selecting a reference site on the same rock type, but remote from human activities. Some data is available from another study of soil contamination carried out around Vanda Station, some 30 km to the west, formed on rocks broadly similar to those at Marble Point (Sheppard *et al.* 1994). Using a

Table V. Results of sequential extractions of lead, zinc and copper from the site on the edge of the rubbish dump at Marble Point (580), at the fire site at Marble Point (582) and the site at Scott Base (601). Concentrations in $\mu\text{g g}^{-1}$.

	sample	depth cm	exchg.	carbonate	oxide	organic
Pb	Under rusty cans, Marble Point					
	580a	0-2	<0.1	0.94	0.70	5.9
	580b	0-2	<0.1	0.1	1.43	0.7
	Site of fire, Marble Point					
	582b	0-3	4.3	7.9	32	126
	582c	3-10	<0.1	<0.1	0.21	<0.1
	583d	10-16	<0.1	0.11	0.21	0.12
	By door, old mess hut site, Scott Base					
	601a	0-1	0.26	6.6	33	37
	601b	1-8	0.1	5.3	9.0	36
	601c	8-19	<0.1	0.56	0.78	1.2
	601d	19-29	<0.1	0.12	0.17	0.51
Zn	Under rusty cans, Marble Point					
	580a	0-2	2.7	14	81	32
	580b	0-2	2.5	9.6	34	15
	Site of fire, Marble Point					
	582b	0-3	94	87	1080	415
	582c	3-10	0.16	1.3	6.7	1.02
	583d	10-16	0.22	1.2	5.5	1.47
	By door, old mess hut site, Scott Base					
	601a	0-1	2.3	62	67	24
	601b	1-8	11.25	61	139	47
	601c	8-19	0.61	3.1	3.7	3.7
	601d	19-29	0.17	5.1	22	7.2
Cu	Under rusty cans, Marble Point					
	580a	0-2	<0.04	0.80	1.24	2.9
	580b	0-2	<0.04	0.40	0.35	0.53
	Site of fire, Marble Point					
	582b	0-3	1.84	4.7	1.8	5.1
	582c	3-10	0.40	0.61	0.11	0.34
	583d	10-16	0.15	<0.04	0.11	<0.18
	By door, old mess hut site, Scott Base					
	601a	0-1	0.14	0.89	0.41	2.0
	601b	1-8	2.2	6.4	1.7	5.2
	601c	8-19	0.57	0.50	1.3	1.2
	601d	19-29	0.14	0.70	0.6	0.3

complexing technique similar to that used for extracting oxide-held elements used here, background levels of $0.4 \mu\text{g g}^{-1}$ Pb were found.

Lead is found in significant amounts near a crushed lead/acid battery, where it is associated with carbonates and oxides. Lead/acid batteries contain lead as a paste of lead oxide in metallic lead, and also as lead ions in solution in the sulphuric acid electrolyte. Thus lead oxide was mechanically added to the soil surface, where it could be transported laterally by wind or downward by water or mechanical mixing. It is not clear whether the site was disturbed during the crushing of the battery, or whether lead oxide particles have been moved through the soil by water from melting snow. Lead in the ionic form is found in the soil, either on the exchange complex of the very small clay

fraction, or associated with soluble salts. It also occurs as carbonate or hydroxycarbonate, formed by precipitation of lead ions by carbonate in the alkaline soil. Lead in the ionic form is more readily mobile and has accumulated at the permafrost surface, a barrier to downward moving moisture.

Zinc

Zinc is present in higher concentrations than lead in the reference site, about $1.4 \mu\text{g g}^{-1}$, largely as oxide. It is possible that these levels represent some contamination. Sheppard *et al.* (1994) found levels of $0.3 \mu\text{g g}^{-1}$ Zn in soils from Vanda Station.

Zinc is found in relatively high concentrations associated with the lead battery. Its origin is unknown, but it may be associated with the lead in the battery itself, or with associated wiring. It is present at elevated levels in soils under copper wire, where it may originate from brass associated with the wire. Copper wire is usually extremely pure for electrical use, but brass is commonly used for fittings, terminals, etc. which may have been present. Of the three heavy metals studied zinc is present in highest amounts in the rubbish dump sites and in the site at Scott Base. It probably originates in the rubbish from protective coatings on steel, (plate, wire or nails, especially the latter); very large amounts of zinc oxide are found in the ashes of the fire site.

Zinc is relatively mobile, moving down the soil profile to accumulate at the interface between the loose soil and the ice-cemented material beneath (sites 579 and 601). It is present in only minor amounts in the more mobile exchangeable or ionic form, and presumably this is rapidly converted to the more stable carbonate or oxide forms.

Copper

Copper is present at all of the sites studied. At the reference site it is associated with the organic fraction, which may indicate an association of copper with the traces of organic matter present in the soil. Since Sheppard *et al.* (1994) found comparable amounts of copper ($1.5 \mu\text{g g}^{-1}$) in soils from undisturbed sites remote from Vanda Station, the values found are probably representative of uncontaminated sites.

Except where copper is obviously present, such as under copper wire, it is not an important contaminant of the soils studied. At the lead battery site, copper levels are similar to those at the reference site, while they are slightly enhanced at the rubbish dump sites and at Scott Base. It is not a very mobile constituent, and appears to remain close to its source. Presumably the major source of copper contamination of the soils is scrap copper from wire, pipe, etc.

Conclusions

This study has shown that traces of heavy metal contamination arising from human activity can be detected in Antarctic soils. Lead, zinc and copper were found close to point sources, such as crushed batteries, scattered rubbish and buildings.

The contaminants are relatively immobile. In 32 years, lead moved less than 50 cm laterally from a battery source and a little over 50 cm vertically from the source. This movement may be attributed to movement in the ionic form, and as oxide particles. Much of the lead is present as oxide. There are some indications that there may also be a more widespread contamination with lead as a result of burning of fuel.

The most widespread contaminant is zinc, which is dissolved from protective coatings on steel, or from paints. Being the most reactive of the three metal contaminants studied, it is the most mobile, and can accumulate at the base of the active layer of the soil. It is found mainly in rubbish dump sites or associated with buildings.

The levels found are not considered to represent serious pollution, but do indicate that human activities can change the chemistry of the Antarctic environment in localized areas.

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