

GREENPEACE, QMC: TECHNICAL NOTE

TRACE METALS IN SOILS AND  
EFFLUENTS FROM ANTARCTICA

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## INTRODUCTION

Trace metals have been extensively investigated in a variety of ecosystems. Whilst some, for example copper and zinc, are a component of biological systems, others such as cadmium have no known biological role. The environmental mobilisation of trace metals as a result of human activity is of concern given the known deleterious effects of these substances upon biological systems (see e.g. Train 1979). In excess, trace metals are known to interfere with a wide range of biochemical functions (Brown & Kodama 1987). The biological availability of metals in aquatic systems depends upon the chemical form in which they are present. This is significantly dependent upon the properties of sediments in an area subject to contamination (Batley & Gardner 1978).

The effects of trace metals on marine and estuarine organisms in temperate regions have been extensively studied (see e.g. Bryan 1971). Direct toxic effects have been described at sufficiently elevated levels. In general, larval forms of organisms are more sensitive to the toxic effects of metals. Connor (1972) found that the larval stages of oysters, shrimp, crab and lobster were between 14 and 1000 times more sensitive to toxic metal effects than adults of the same species. He concluded that the continued addition of copper, mercury and zinc to confined waters should give cause for concern. Sub-lethal effects are also of importance. For example, Johnston (1987) found that egg production in a freshwater cladoceran was significantly reduced by exposure to selenium at sub-acute levels and that reproductive maturity was delayed.

Although there is evidence that some animal communities may adapt to elevated levels of trace metals (Bryan 1976), the accumulation and storage of metabolically inert forms (Rainbow 1988; Hamilton & Mehrle 1986) may lead to wider problems. Bryan (1971) notes that in the case of some marine animals, relatively small elevations in trace metal levels in the environment can result in high accumulated levels. This is particularly true in the case of sediment dwelling benthic organisms. The metals thus have the potential to enter the food chain. Scheuhammer (1987) reviewed the chronic toxicity of dietary metal exposure in bird species and concluded that significant physiological and biochemical responses occur at dietary metal levels insufficient to cause signs of overt toxicity. Reproductive effects such as decreased egg production, lowered hatchability and increased hatchling mortality were regarded as particularly important.

Recently, (Nriagu & Pacyna 1988; Nriagu 1988) attention

has been drawn to the global significance of heavy metal mobilisation. The total toxicity of all heavy metal emissions as indexed by the quantity of water required to dilute them to drinking water standards is thought to exceed the toxicity of organic and radioactive wastes combined.

Trace metal contamination in marine systems, by affecting the reproductive success of a wide variety of organisms may therefore seriously disturb the structure of the contaminated ecosystem. Much of the research on trace metal contaminants has been conducted on temperate and tropical marine systems. Few data have been published for Antarctic systems. The unique environmental conditions in Antarctic areas may possibly result in modifications to the cycling of metals which may be of toxicological significance. Given the current poor understanding of metal behaviour in Antarctic systems the mobilisation of these substances must be viewed with extreme concern.

The results reported here are for metal levels in effluents and soils from the US Antarctic base at McMurdo Sound and the New Zealand Scott Base.

#### METHODS

Effluent samples were taken in acid washed glass bottles and acidified by addition of 20% by volume of hydrochloric acid to ensure good long term preservation. Soil samples were taken from areas of interest and stored frozen in polythene containers. Soil samples were transported frozen to the laboratory for analysis.

Aqueous samples were determined for metals directly using flame atomic absorption spectrophotometry on an IL 157 machine with background correction. Soil samples were subjected to wet ashing using ARISTAR grade concentrated nitric acid followed by centrifugation. Analysis was carried out on a portion of digest diluted with double glass distilled water. To ensure quality control similar preparations of a pond sediment reference material were analysed at the same time (NIES certified reference material, Japan Environment Agency).

#### RESULTS

Results for trace metal analyses of soils and effluents together with sampling locations and dates are tabulated below. Effluent metal levels are corrected for the addition of the preserving acid. Locations for 1987/88 are also shown on the attached map of the area.

SAMPLE	Cd	Cu	Pb	Zn	Cr	Ag	DETECTION LIMITS: SOILS ppm AQUEOUS ppm
	0.05 0.01	0.05 0.01	1.0 0.2	0.05 0.01	0.1 0.02	0.025 0.005	
1986/87							LOCATION
009S	0.37	43.5	27.0	32.55	16.4	N/D	Transformer storage area McMurdo. 9/2/87
010S	0.75	28.7	4.5	32.5	17.7	N/D	
011S	N/D	47.9	1.5	30.2	13.0	N/D	
012S	N/D	37.3	3.0	30.7	12.2	N/D	
013S	0.35	20.0	24.5	32.1	13.8	N/D	
014S	0.35	31.6	18.2	31.85	15.1	N/D	
015S	0.43	21.0	80.0	36.7	16.7	N/D	
017S	0.31	16.4	21.0	32.0	16.5	N/D	
020S	0.33	8.0	17.5	29.8	12.4	N/D	
022S	0.6	30.5	43.0	34.1	11.9	0.18	
023S	0.30	31.8	22.5	31.2	11.3	N/D	McMurdo, sewage outfalls
006A	N/D	0.71	N/D	0.21	N/D	N/D	
007A	N/D	N/D	N/D	N/D	0.04	N/D	
025S	0.45	24.0	64.5	29.7	10.6	0.945	Scott base, sewage o/f photolab, surf.water sewage outfall sewage outfall
027A	N/D	0.82	N/D	0.15	N/D	0.075	
028A	N/D	0.09	N/D	0.03	N/D	N/D	
029A	N/D	0.73	N/D	0.32	0.016	N/D	

S denotes soil sample, A denotes aqueous sample. N/D: not detected  
All values given in ppm dry weight for soils, mg/l for aqueous samples.

TABLE 1: Metal content of soils and aqueous samples taken at McMurdo  
and Scott Bases. (1986/7)



SAMPLE	Cd	Cu	Pb	Zn	Cr	Ag	LOCATION
001S (1)	0.78	31.5	32.5	56.8	62.7	N/D	McM dump creek
002S (2)	0.90	32.5	37.1	65.4	74.3	N/D	McM transformer store
003S (2)	0.80	15.4	19.4	48.0	11.0	N/D	McM transformer store
004S (2)	0.81	18.9	22.4	53.1	11.6	N/D	McM transformer store
005S (4)	0.60	4.0	N/D	46.0	1.8	N/D	McM near sewage o/f
006S (4)	1.45	49.8	165.8	89.5	82.9	N/D	dump near sewage o/f
007S (4)	N/D	2.04	13.7	14.7	2.0	1.04	battery and metal dump
008S (5)	0.75	16.8	27.9	58.4	5.1	N/D	pond sediment nr. o/f
009S (7)	N/D	1.0	40.2	2.4	1.8	N/D	Scott Bs. photolab outlet
010S (8)	0.57	31.1	3.1	65.3	65.8	21.4	spill site
011S (10)	N/D	29.4	1.2	44.8	4.5	3.26	near incinerator
012S (11)	N/D	10.8	882.0	600.0	7.4	N/D	leaking fuel tank
013S (14)	0.56	43.5	18.6	60.3	113.2	N/D	McM dumpsite
014S (14)	N/D	33.3	63.9	69.8	98.1	N/D	McM near dumpsite
015S (15)	N/D	30.0	10.7	61.8	67.6	N/D	McM battery store
001CA (1)	N/D	0.18	0.07	0.11	---	N/D	McM Surf. water, main St
002CA (3)	0.01	0.15	0.05	0.11	---	N/D	McM Ponds at old dump
003CA (5)	0.41	0.15	0.36	0.31	---	0.03	McM new sewage o/f
004CA (6)	0.55	0.50	0.08	0.10	---	N/D	McM temp. hose o/f
005CA (7)	0.01	0.71	0.18	0.32	---	1.42	Scott: photo lab pond
006CA (9)	0.34	7.68	0.15	0.58	---	0.05	Scott: sewage o/f
007CA (13)	N/D	0.06	N/D	0.07	---	N/D	Scott/McM roadside lak

Detection limits as in TABLE 1 except for lead in aqueous samples: 0.02mg/l. o/f: outfall. Numbers in parentheses refer to localities shown on the map appended as Figure 1. All values given as ppm dry weight for soil samples and mg/l for aqueous samples.

TABLE 2: Metal levels in soils and aqueous samples taken in the vicinity of McMurdo and Scott bases 1987/88.

A:	Cd	Cu	Pb	Zn	Cr	Ag
Mean	0.35	28.7	23.8	32.1	14.27	----
SD	0.20	11.82	22.18	1.92	2.27	----
Mean +3(SD)	0.95	64.16	90.34	37.9	21.08	----
Range	<0.05-0.60	8.0-47.9	1.5-80.0	29.8-36.7	11.3-17.7	----
B:						
Mean	0.50	23.36	89.3	89.08	40.65	----
SD	0.43	14.89	223.0	142.9	40.74	----
Mean + 3(SD)	1.79	68.03	758.3	517.7	162.8	----
Range	<0.05-1.45	1.0-49.8	<1.0-882.0	2.4-600.0	1.8-113.2	

TABLE 3: Statistics relating to soil samples taken at McMurdo and Scott bases. All figures in ppm dry weight. A: 1986/87 B: 1987/88 Silver values not calculated

## DISCUSSION

The analytical results reported above suggest that significant mobilisation of heavy metals is taking place into the Antarctic environment as a result of the activities of the Scott and McMurdo bases. For the purposes of comparison, soil samples taken from the transformer storage area at McMurdo Base during 1986/7 were treated as a "baseline set". Such an approach seems justified given the consistency of the values obtained from the metal determinations. These seem to indicate little metal contamination of the soil. Although casual inspection of the soil samples taken during 1987/88 suggests that they are similarly derived, much greater variation in metal values is evident. This suggests some differences between sites possibly due to different environmental conditions affecting metal mobility. Soil properties are currently under investigation. Consequently anthropogenic source attribution of the metals found is uncertain except in the case of extremely elevated values. Work is currently in progress to rectify this problem.

### a) Silver

Aqueous samples obtained during the 1986/87 season indicate appreciable releases of silver (Sample 027A:86/87) and this is reflected in elevated soil silver levels close to pipes (Sample 025S:86/87). Silver was also detected in samples taken during 1987/88. 0.03ppm was found in the new sewage discharge from McMurdo (Sample 003CA:87/88) and 1.42 ppm in aqueous Sample 005CA:87/88 from a pond associated with the Scott Base photolab. Soil samples from McMurdo (Sample 007S:87/88) showed elevated silver levels whilst an apparent spill site at Scott Base (Sample 010S:87/88) had the extremely high level of 21.4ppm. Sample 011S contained 3.26ppm. It seems likely that silver contamination has resulted from the disposal of photographic chemicals. Certainly, it seems unlikely that the recorded level of 21.4ppm could have arisen as a result of minor, accidental spillage.

Silver is biologically extremely potent. Dosages of 0.001-500ug/l of silver have been reported as effective in water sterilization (McKee & Wolf 1963). It is likely that silver emissions will seriously impact the soil microflora in receiving areas. There is a wide reported variability in the toxicity of silver to aquatic organisms. The silver criterion for water quality is therefore set at 0.01 of the 96HLC50 as determined using a



sensitive resident species (NAS 1974). This application factor is recommended for persistent or cumulative toxicants. We are not aware of any bioassay data for silver using Antarctic organisms. Further, current practical recommendations suggest the retrograding of photographic wastes. Accordingly, silver emissions should be tightly controlled in Antarctic environments.

#### b) Cadmium

Cadmium has no known biological function and has been found to interfere with the reproductive processes of freshwater organisms at levels as low as 12ug/l (Griffiths 1983). Cadmium is known to be cytotoxic although the precise toxic mechanisms are not well understood (Aoki et al. 1987). As a result of increasing concern about cadmium in the environment, stringent regulation of discharges has been imposed in the European Community (OJ No: L74, 17.3.1984). As such, it is designated as a List I substance for the purposes of the dangerous substances directive (Directive 76/464/EEC, Annex. OJ L 129, 18.5.76). This sets an effective ceiling of 0.5ppm Cd in discharges as of 1.1.86 due to be reduced to 0.2ppm as of 1.1.89. Samples taken of sewage effluents at both McMurdo and Scott Bases showed appreciable discharge of cadmium. In the case of Sample 004CA:87/88 from a temporary discharge hose, the value of 0.55ppm is in clear breach of standards set for industry in European countries. Samples 003CA:87/88 & 006CA:87/88 are in excess of the values applicable in the EEC from 1.1.89. (Gardiner & Mance 1984).

The source of the cadmium found in the sewage effluents is not clear. Clearly however the discharge of quantities of this metal more normally associated with industrial production into a pristine environment is unacceptable. Control measures should be implemented as a matter of urgency.

Soil samples showed a level of cadmium generally consistent with reported soil contents. A slight elevation of Cd level is apparent in a soil sample taken from the old dumpsite at McMurdo near the sewage outfall (Sample 006S:87/88). The value of 1.45ppm cannot however be regarded as statistically anomalous where such values are defined as those lying outside three standard deviations of the arithmetic mean.

#### c) Lead

The toxic properties of lead are now well known (See: Train 1979; Braithwaite & Brown 1987; Nriagu 1988). The lead levels found in the soil samples taken at McMurdo Base in 1986/7 suggest a mean background level of 23.8ppm

which is consistent with normal levels reported in soils. Some elevation of lead level is indicated by the 80ppm present in sample 015S:86/87 but the value is not statistically anomalous. This must therefore be regarded as at worst slightly contaminated using the broad guidelines defined by Lux et al. (1988). Sample 012S:87/88 taken near a leaking fuel tank shows a statistically anomalous value of 882.0ppm of lead. Applying the guidelines above this soil must be regarded as extremely contaminated. This is defined as a soil lead level in excess of 500ppm. The mean metal levels reported by Lux et al. (1988) for the Hamburg area are higher than those reported here as would be expected for an industrialised and urbanised area. Blake et al. (1987) reported lead levels of 4590ppm in soils from a car breakers yard in the UK. The values reported here for a "pristine" area are therefore some 20% of those arising from a highly contaminating industrial sector.

The anomalous lead value found at Scott base may therefore be regarded as indicative of extreme contamination. Schlipkoter & Brockhaus (1988) cite a threshold level for lead in soil of 300ppm for unrestricted use. Values cited by Lux et al. (1988) range from 50-600ppm. The latter value is regarded as the "C" value in the Netherlands, (Debruijn & DeWalle 1988) at which removal/decontamination of the soil is recommended.

In the case of metal contaminated soils in the Antarctic environment, removal is the preferred option. Versluijs et al. (1988) note that while some clean-up techniques may lower the overall metal burden, this may be at the expense of increased metal mobility and bioavailability in the soil thus making the problem worse in environmental terms.

Lead levels determined in effluents sampled from both bases were generally consistent with a normal sewage content of 0.01-0.05 ppm (Brown et al. 1984) except in the case of sample 003CA:87/88 which contained 0.36ppm. The high level of cadmium and the presence of silver in this discharge suggest together that this pipeline is used for the discharge of workshop and/or laboratory wastes.

#### d) Zinc

Zinc levels found in the analysed soil samples were generally within the range expected in a soil. Levels found in 87/88 samples showed a greater range than those taken in 86/87 even when the anomalous value of 600.0ppm in sample 012S:87/88 was excluded. Samples taken at the McMurdo transformer storage site in 87/88 had elevated levels of zinc as compared with 86/87 samples. Levels of other metals were comparable although slight apparent



elevation is evident for sample 002S:87/88 with respect for chrome. The anomalous zinc value is somewhat greater than those given by Blake et al. for a car breakers yard (mean value 554ppm). It is however only a "B" limiting value according to the Netherlands classification scheme. This would require more extensive evaluation to ascertain whether clean-up was required. Moderately high levels were found in effluent samples from both Scott and McMurdo bases suggesting that these sewage outfalls discharge a combined domestic/industrial effluent. Domestic sewage normally contains approximately 0.2ppm of zinc (Mance & Yates 1984).

#### e) Copper

Copper is normally present in sewage effluents at levels of approximately 0.15ppm (Mance et al. 1984). The values of copper reported for aqueous samples from Scott and McMurdo bases markedly exceed this value in samples 027A:86/87, 029A:86/87, 004CA:87/88, 005CA:87/88, 006CA:87/88. In the case of sample 006CA 87/88, 7.6ppm was detected. This level would more usually be associated with industrial activity and is some 50 times the level expected in normal domestic sewage. No evidence was found of elevated copper levels in soil samples analysed.

#### f) Chromium

Elevated levels of chromium are suggested by the value of 113.2ppm found in soil sample 013S:87/88. This was taken from the McMurdo dumpsite and is probably due to scrap metal.

### CONCLUSIONS

The results suggest that appreciable anthropogenic mobilisation of heavy metals is taking place in the areas of Scott and McMurdo bases. This has resulted in significant contamination of soils in some areas. Effluents from the bases also contain significant amounts of metals. Effluent loadings are consistent in some cases with those expected from a combined effluent rather than from domestic sewage alone. The toxicological implications of metal contaminant mobilisation remain unevaluated in the area but may have implications for local bird populations in terms of food chain transfer. It is desirable to both minimise future effluent discharges and remove for decontamination soils in the areas affected to ensure adequate protection of the environment.

Necessary future work will involve the following:

- 1) An evaluation of soil metal levels based on a near and far field grid.

- 2) An evaluation of metal levels in biological materials in the vicinity of both bases.
- 3) An evaluation of sediment load of metals in the vicinity of both bases and from control areas.
- 4) Evaluation of the toxicological implications of the aquatic discharges.

Points 1-3 will be addressed by the Greenpeace overwintering team during the 1988/89 season. It is also hoped that an evaluation of organic contaminants will be made. Point 4 will involve considerable research work, given the currently poor understanding of Antarctic ecosystems. Funding must be made available for this work.

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