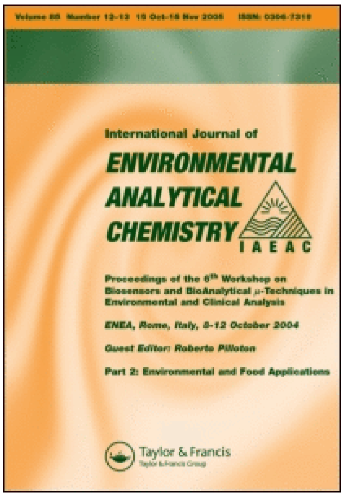

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# Determination of Trace Metals in Antarctic Sediments from Terra Nova Bay - Ross Sea

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# DETERMINATION OF TRACE METALS IN ANTARCTIC SEDIMENTS FROM TERRA NOVA BAY - ROSS SEA

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Trace metals (Cu, Pb, Zn, Cd, Cr, Ni, Co, Mn) and iron concentration were determined in several sediments collected in the Antarctica (Terra Nova Bay—Ross Sea). Samples were analyzed by inductively coupled plasma (ICP-AES) after selective and total extraction. The results are in good agreement with the data previously collected in the same area.

**KEY WORDS:** Trace metals, sediments, Antarctica, sequential extraction, ICP-AES.

## INTRODUCTION

The analysis of trace metals and their distribution in marine sediments is a very important step towards understanding geochemical and environmental processes and their possible changes due to anthropogenic activities [1]. It is well-known that the determination of trace metal in sediments presents a number of complex problems due to the different possible binding metals in the phases within the sediment [2,3,4].

Many extraction methods, are proposed for determining the metal concentrations, in various sediment phases (exchangeable, easy or moderately reducible, organic and residual) which characterize accumulation sites and bioavailability of metal in the marine ecosystem [5,6].

In our contribution to the Antarctica Project—Sector Environmental Impact—Analytical Methodologies, we have undertaken a study on the determination and the distribution of trace metals in superficial sediments of the Antarctica ecosystem. This information is indispensable for determining the possible environmental impact that the Italian Antarctic Base may have on the marine ecosystem of Terra Nova Bay.

The present paper shows the results concerning the trace metal analysis for Cu, Pb, Zn, Cd, Cr, Ni, Co, Mn and Fe as macroelement in sediments collected by the Italian expedition in Terra Nova Bay—Ross Sea in 1989/90 and aims to confront these results with those of previous expeditions (1987/88) in the same area [7,8].

## EXPERIMENTAL

### *Materials*

During the Italian expedition in Terra Nova Bay—Antarctica—1989/1990, twenty-two of sediment samples were collected along the coast with a stainless steel grab.

Immediately after sampling all the samples were frozen at –24°C. The samples were collected in a restricted coastal zone adjacent to the Italian base of Terra Nova Bay at low water depth (0.5 m + 368 m) except at stations 36, 42, 48, where the water depth was 516, 540 and 495 m, respectively.

The geographical parameters are shown in Table 1.

## APPARATUS

### *Instrumentation*

A Jobin Yvon (Longjumeau—Paris, France), JY 24 inductively coupled plasma atomic emission spectrometer equipped with a Reyton 2300 RF plasma torch fitted with Scott glass

TABLE 1 Geological location of sediment samples collected in Terra Nova Bay (Antarctica)

| Sample | Depth (m) | South Lat. | East Long. |
|---|---|---|---|
| 12 | 0.5 | 74° 18.00' | 165° 05.00' |
| 21 | 0.5 | 74° 50.00' | 163° 55.00' |
| 23 | 23 | 74° 42.97' | 164° 06.90' |
| 24 | 368 | 74° 40.66' | 164° 09.76' |
| 27 | 260 | 74° 45.50' | 164° 15.90' |
| 28 | 112 | 74° 45.20' | 164° 06.50' |
| 28 | 330 | 74° 45.50' | 164° 19.30' |
| 30 | 273 | 74° 52.36' | 164° 16.21' |
| 31 | 275 | 74° 51.87' | 164° 08.61' |
| 32 | 274 | 74° 54.20' | 164° 11.49' |
| 33 | 105 | 74° 30.07' | 164° 10.70' |
| 34 | 194 | 74° 38.55' | 164° 10.52' |
| 35 | 300 | 74° 39.07' | 164° 09.93' |
| 36 | 516 | 74° 40.23' | 164° 12.17' |
| 37 | 362 | 74° 40.01' | 164° 20.21' |
| 38 | 228 | 74° 46.47' | 164° 11.58' |
| 39 | 175 | 74° 46.12' | 164° 08.23' |
| 41 | 454 | 74° 40.99' | 164° 22.57' |
| 42 | 540 | 74° 42.71' | 164° 16.92' |
| 45 | 113 | 74° 44.51' | 164° 08.01' |
| 46 | 295 | 74° 44.32' | 164° 12.84' |
| 48 | 495 | 74° 43.28' | 164° 16.88' |

spray chamber and a Meinhard concentric glass nebuliser supplied by a Gilson IIA peristaltic pump was used.

### *Reagents*

- 1000 $\mu g g^{-1}$ standard solutions spectrosol grade, BDH CHEMICALS Ltd Poole, England.

- Water used through out the experiment was nanopure grade, produced by a Milli-Q Water System (Millipore).

- All chemical reagents were analytical grade (C. Erba, Italy, Analyticals RPE).

- Glass and plastic (PTFE) vessels were washed with diluted nitric acid and rinsed with nanopure water.

### *Procedures*

*Total metal solubilization.* A representative unfrozen sample of 0.5 g, dried at 110°C and finely powdered, was dissolved in a teflon bomb (Perkin-Elmer, Italy) in an acid mixture of 5 ml of 40% HF, 1 ml of aqua regia ($HNO_3$—HCl 1:3 v/v) and 5 ml of Milly-Q water. Five ml of saturated $H_3 BO_3$ solution were then added to the teflon bomb which had been previously heated to 180°C for an hour and a half and then cooled to room temperature.

After dilution to 50 ml in a volumetric flask, the solution was analyzed by ICP-AES [8].

### *Selective metal solubilization*

5 g of finely powdered sediment dried at 45°C were subsequently shaken with a different water solution in order to obtain selective metal solubilization, as summarizes in the diagram in Figure 1. The metal content in the three solutions was then determined by ICP-AES: "A": metals present in ionic exchanging form and in the carbonate fraction, "B": metals present in the reductive phase bound to Fe-Mn oxides and "C": metals bound to sulphide and to the organic phase [8].

To test the precision and accuracy of the total solubilization method, we analyzed two international standard sediments (MAG-1; U.S. Geological Survey. BCSS-1; National Research Council of Canada). The results obtained are in good agreement with certified values [9].

## RESULTS

In Table 2 the total and mean values of Cu, Pb, Zn, Cd, Fe, Cr, Ni, Co and Mn determined

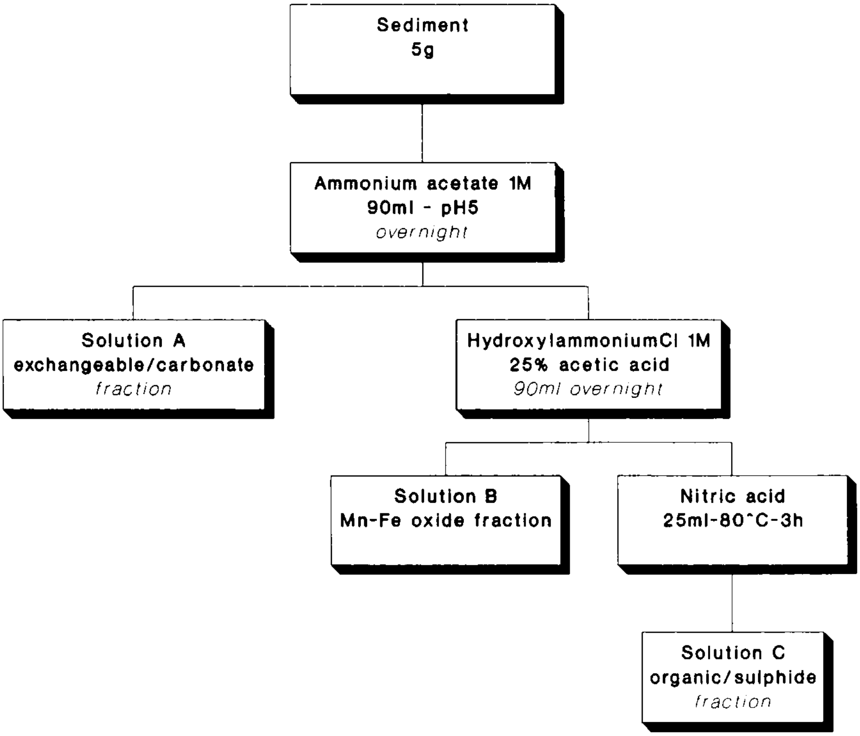

**Figure 1** Diagram of selective extraction procedure.

in twenty-two sediments from Antarctica are reported. In general, the trace metal content of these sediments, is sufficiently different for each samples.

The concentration of copper has mean value of 25.3 μgg$^{-1}$ (range 16.2 ÷ 53.5 μgg$^{-1}$). The values of Pb are sufficiently uniform (range 8.25 ÷ 17.3 μgg$^{-1}$ and average 12.7 μgg$^{-1}$).

Zinc presents a mean value of 108 μgg$^{-1}$ and a range of 60.4 ÷ 231 μgg$^{-1}$. The mean value of cadmium is 0.30 μgg$^{-1}$ and its values are quite uniform (range 0.10 ÷ 0.58 μgg$^{-1}$).

The values of Cr are sufficiently uniform for all samples (range 14.1 ÷ 37.6 μgg$^{-1}$) and the total mean value (27.7 μgg$^{-1}$) is lower than that reported by us in the same antarctic zone [8].

For nickel, the mean value is 24.2 μgg$^{-1}$ with a range 10.2 ÷ 59.9 μgg$^{-1}$. The cobalt concentration is quite uniform for all samples, with values varying from 4.11 to 18.5 μgg;$^{-1}$ and a mean value of 5.80 μgg$^{-1}$. For Mn and Fe, the mean values are in good agreement with the available data.

The results of the selective extraction of eight representative samples (12, 21, 23, 29, 32, 33, 34 and 41) and the total concentrations are reported in Table 3. In Table 4, the mean values and percentages of the total concentration for the same samples are shown. Generally, the extraction efficiency of each A,B,C reagent depends on the acid strength [10] and on the oxidizing or reducing power of the same solution. This extraction efficiency is in increasing order going from the A to the C reagent [10].

TABLE 2 - Total concentration of the metals ($\mu g g^{-1}$) in the antarctica sediments

| Station | Cu | Pb | Zn | Cd | Cr | Ni | Co | Mn | Fe |
|---|---|---|---|---|---|---|---|---|---|
| 12 | 28.3 | 8.25 | 166 | 0.15 | 14.1 | 22.5 | 18.5 | $1.20\ 10^3$ | $6.05\ 10^4$ |
| 21 | 16.2 | 12.9 | 102 | 0.10 | 33.0 | 16.4 | 6.79 | 402 | $2.15\ 10^4$ |
| 23 | 30.7 | 10.3 | 144 | 0.10 | 17.3 | 16.2 | 6.62 | 452 | $2.32\ 10^4$ |
| 24 | 44.1 | 13.9 | 109 | 0.50 | 24.5 | 10.7 | 5.34 | 587 | $1.91\ 10^4$ |
| 27 | 35.0 | 16.9 | 198 | 0.58 | 28.2 | 18.0 | 4.33 | 728 | $1.93\ 10^4$ |
| 28 | 53.5 | 11.2 | 231 | 0.35 | 31.7 | 19.5 | 6.70 | 702 | $2.90\ 10^4$ |
| 29 | 30.4 | 11.9 | 154 | 0.20 | 27.4 | 15.1 | 4.11 | 728 | $1.72\ 10^4$ |
| 30 | 28.2 | 13.3 | 108 | 0.22 | 30.2 | 28.8 | 8.08 | 390 | $2.14\ 10^4$ |
| 31 | 19.6 | 13.5 | 91.6 | 0.36 | 29.1 | 32.4 | 4.53 | 530 | $1.83\ 10^4$ |
| 32 | 33.5 | 14.7 | 117 | 0.15 | 37.6 | 59.9 | 7.24 | 422 | $2.40\ 10^4$ |
| 33 | 26.7 | 13.3 | 89.4 | 0.70 | 36.5 | 39.6 | 4.25 | 599 | $1.80\ 10^4$ |
| 34 | 21.8 | 16.5 | 82.3 | 0.35 | 27.3 | 49.3 | 3.22 | 646 | $1.52\ 10^4$ |
| 35 | 37.1 | 13.9 | 107 | 0.48 | 23.2 | 12.2 | 5.27 | 568 | $1.72\ 10^4$ |
| 36 | 25.0 | 14.6 | 81.6 | 0.30 | 24.4 | 11.0 | 4.30 | 600 | $1.82\ 10^4$ |
| 37 | 22.2 | 14.1 | 71.5 | 0.28 | 25.1 | 10.2 | 4.66 | 596 | $1.76\ 10^4$ |
| 38 | 26.3 | 17.3 | 87.3 | 0.43 | 26.0 | 12.5 | 4.55 | 553 | $1.84\ 10^4$ |
| 39 | 35.4 | 14.9 | 99.1 | 0.23 | 29.0 | 15.8 | 5.22 | 514 | $2.12\ 10^4$ |
| 41 | 21.2 | 11.9 | 68.4 | 0.22 | 26.5 | 20.6 | 5.51 | 503 | $1.60\ 10^4$ |
| 42 | 23.1 | 9.45 | 74.6 | 0.30 | 28.2 | 26.4 | 4.33 | 448 | $1.81\ 10^4$ |
| 45 | 16.7 | 10.0 | 69.3 | 0.22 | 29.1 | 16.8 | 4.54 | 646 | $2.50\ 10^4$ |
| 46 | 18.0 | 8.25 | 60.4 | 0.30 | 28.4 | 33.2 | 5.37 | 678 | $2.13\ 10^4$ |
| 48 | 17.5 | 9.10 | 61.2 | 0.17 | 32.3 | 45.1 | 4.08 | 394 | $2.15\ 10^4$ |
| Mean value | 25.3 | 12.7 | 108 | 0.30 | 27.7 | 24.2 | 5.80 | 586 | $2.16\ 10^4$ |

TABLE 3 - Concentration of the metals ($\mu g g^{-1}$) extracted by the reagents A, B, C and T

| Station | Reag*. | Zn | Pb | Ni | Cd | Co | Fe | Cr | Mn | Cu |
|---|---|---|---|---|---|---|---|---|---|---|
| 12 | A | 2.51 | 1.09 | 0.31 | 0.02 | 0.28 | 65 | 0.05 | 14.8 | 0.88 |
| | B | 8.34 | 0.78 | 2.25 | 0.01 | 2.47 | $5.20\ 10^3$ | 0.52 | 113 | 1.22 |
| | C | 50.5 | 5.80 | 7.42 | 0.04 | 15.5 | $3.25\ 10^4$ | 4.46 | 656 | 7.59 |
| | T | 166 | 8.25 | 22.5 | 0.15 | 18.5 | $6.05\ 10^4$ | 14.1 | $1.20\ 10^3$ | 28.3 |
| 21 | A | 2.42 | 1.11 | 0.59 | 0.03 | 0.24 | 69 | 0.20 | 6.36 | 1.14 |
| | B | 1.82 | 1.38 | 1.15 | 0.04 | 0.58 | 513 | 0.47 | 8.26 | 0.81 |
| | C | 33.5 | 10.2 | 5.43 | 0.02 | 5.55 | $1.71\ 10^4$ | 19.8 | 237 | 7.54 |
| | T | 102 | 12.9 | 16.4 | 0.10 | 6.79 | $2.15\ 10^4$ | 33.0 | 402 | 16.2 |
| 23 | A | 5.61 | 0.29 | 0.53 | 0.04 | 0.11 | 46 | 0.20 | 1.84 | 0.50 |
| | B | 2.52 | 0.81 | 0.79 | 0.02 | 0.35 | 445 | 0.43 | 5.70 | 0.35 |
| | C | 24.6 | 8.5 | 4.67 | 0.02 | 6.08 | $1.27\ 10^4$ | 8.20 | 102 | 5.18 |
| | T | 144 | 10.3 | 16.2 | 0.10 | 6.60 | $2.32\ 10^4$ | 17.3 | 452 | 30.7 |
| 29 | A | 3.45 | 0.07 | 0.70 | 0.14 | 0.16 | 10 | 0.25 | 0.83 | 0.51 |
| | B | 3.07 | 0.45 | 1.13 | 0.01 | 0.29 | 354 | 0.45 | 8.97 | 0.28 |
| | C | 20.5 | 10.6 | 3.15 | 0.03 | 2.88 | $5.79\ 10^3$ | 5.99 | 92 | 5.83 |
| | T | 154 | 11.9 | 15.1 | 0.20 | 4.11 | $1.72\ 10^4$ | 27.4 | 728 | 30.4 |
| 32 | A | 1.85 | 0.09 | 4.51 | 0.06 | 0.40 | 8 | 0.25 | 10.6 | 0.60 |
| | B | 9.34 | 0.50 | 3.48 | 0.01 | 0.56 | 521 | 0.58 | 15.9 | 0.51 |
| | C | 62.3 | 13.4 | 8.59 | 0.02 | 6.09 | $1.80\ 10^4$ | 14.40 | 237 | 17.2 |
| | T | 117 | 14.7 | 59.9 | 0.15 | 7.24 | $2.40\ 10^4$ | 37.6 | 422 | 33.5 |
| 33 | A | 11.7 | 1.14 | 1.52 | 0.55 | 0.13 | 16 | 0.45 | 5.11 | 0.93 |
| | B | 5.15 | 0.59 | 1.73 | 0.10 | 0.37 | 405 | 0.52 | 7.66 | 0.57 |
| | C | 28.7 | 10.1 | 8.06 | 0.01 | 3.25 | $1.29\ 10^4$ | 16.41 | 188 | 13.1 |
| | T | 89.4 | 13.3 | 39.6 | 0.70 | 4.25 | $1.80\ 10^4$ | 36.5 | 599 | 26.7 |
| 34 | A | 6.32 | 0.13 | 0.49 | 0.28 | 0.13 | 6 | 0.27 | 0.71 | 0.09 |
| | B | 3.62 | 0.62 | 0.92 | 0.01 | 0.24 | 239 | 0.63 | 8.67 | 0.08 |
| | C | 15.7 | 7.34 | 3.33 | 0.02 | 2.68 | $6.20\ 10^3$ | 8.59 | 119 | 6.96 |
| | T | 82.3 | 16.5 | 49.3 | 0.35 | 3.22 | $1.52\ 10^4$ | 27.3 | 646 | 21.8 |
| 41 | A | 8.31 | 1.36 | 0.77 | 0.16 | 0.12 | 9 | 0.36 | 0.59 | 0.42 |
| | B | 3.85 | 0.22 | 1.50 | 0.02 | 0.35 | 406 | 0.52 | 6.10 | 0.22 |
| | C | 21.5 | 6.90 | 4.50 | 0.02 | 2.91 | $6.91\ 10^3$ | 7.75 | 98 | 7.19 |
| | T | 68.4 | 11.9 | 20.6 | 0.22 | 5.51 | $1.60\ 10^4$ | 26.5 | 503 | 21.2 |

*Reagents: A: $CH_3COONH_4$ 1 M pH 5; B: $NH_2OH{\cdot}HCl$ 1 M + $CH_3COOH$ 25% (V:V); C: $HNO_3$ 8N
T: Total attack (HF + Acqua regia - Teflon Bomb).

The same trend occurs in these samples for all metals except for Cd, Pb and Zn. Cadmium shows much higher values for reagent A than for reagent B (64% for reagent A and 12.0% of the total in the reductive phase). Zinc and lead show similar values for the A and B reagents (5.3% and 5.3% respectively for Pb and 4.6% and 4.1% respectively for Zn). Moreover, Pb

TABLE 4 - Mean values of the metals ($\mu g g^{-1}$) and the percentages (%) of the total in sediments (for stations 12, 21, 23, 29, 32, 33, 34 and 41)

| Element | Reagents* | Mean | % of Total | Element | Reagents* | Mean | % of Total |
|---|---|---|---|---|---|---|---|
| Cu | A | 0.63 | 2.5 | Cr | A | 0.25 | 0.9 |
| | B | 2.02 | 7.9 | | B | 0.51 | 1.9 |
| | C | 8.82 | 34.5 | | C | 10.7 | 39.5 |
| | T | 25.6 | | | T | 27.1 | |
| Pb | A | 0.66 | 5.3 | Ni | A | 1.18 | 4.0 |
| | B | 0.67 | 5.3 | | B | 1.62 | 5.5 |
| | C | 9.11 | 72.9 | | C | 5.64 | 19.0 |
| | T | 12.5 | | | T | 29.5 | |
| Zn | A | 5.27 | 4.6 | Co | A | 0.20 | 2.8 |
| | B | 4.71 | 4.1 | | B | 0.65 | 9.3 |
| | C | 31.2 | 27.1 | | C | 5.61 | 80.1 |
| | T | 115 | | | T | 7.00 | |
| Cd | A | 0.16 | 64.0 | Mn | A | 6.10 | 0.8 |
| | B | 0.03 | 12.0 | | B | 21.8 | 3.5 |
| | C | 0.02 | 8.0 | | C | 216 | 34.9 |
| | T | 0.25 | | | T | 619 | |
| Fe | A | 29 | 0.1 | | | | |
| | B | $1.01\ 10^3$ | 4.1 | | | | |
| | C | $1.41\ 10^4$ | 57.8 | | | | |
| | T | $2.44\ 10^4$ | | | | | |

*Reagents: A: $CH_3COONH_4$ 1 M pH 5; B: $NH_2OH{\cdot}HCl$ 1 M + $CH_3COOH$ 25% (V:V); C: $HNO_3$ 8N
T: Total attack (HF + Acqua regia - Teflon Bomb).

and Zn are present as 72.9% and 27.1%, respectively of total content, in the organic and sulphide phases possibly present.

As regards chromium, nickel and manganese, the bulk of the metal is present in residual matrix. The selective reagents A and B show a very small percentages of the total content, but the reagent C shows 39.5%, 19.0% and 34.9% Cr, Ni and Mn respectively, of the total content.

The values of cobalt and iron are 80.1% and 57.8%, respectively, of total content in the organic and sulphide phases; moreover, they both show very low percentages in the carbonate and reductive phases. We noticed a very low percentage of copper for A and B cold solutions and 34.5% of the total for the organic phases.

In order to examine some correlations between the metals, it is interesting to note that, in correlation with total iron, considered as an index of common origin [11], only the pairs of metal Co-Fe and Cr-Fe show significant correlation values $r=0.94$ and $r=0.45$ at 99% and 95% confidence level, respectively. For Zn-Fe, $r=0.62$ at 99% confidence level if we exclude sample 12; in fact, this sample, originates from a different location and has a different mineralogical composition.

## CONCLUSIONS

Significant differences were not observed in the concentrations of metals in sediments collected during successive antarctic expeditions.

The mean values for the metals are generally in good agreement with previously collected data.

The selective extraction procedure usually shows that the exchangeable fraction and that bound to the carbonatic phase (solution A) and the fraction bound to Fe-Mn oxides (solution B) are quite low for all metals, except in the case of Cd, which shows a high value (64.0% of total) for reagent A.

In our opinion, in order to verify the environmental impact influences, it will be necessary to take into account a comparison of analysis results of sediment samples collected over the years.

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