Metal complexation capacity of Antarctic lacustrine sediments

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HIGHLIGHTS

- Determination of metal complexation properties of some natural organic and biologic substances.
- Method applied to Antarctic lacustrine sediments, within a main thematic project on "Chemical Contamination-Global Change".
- Results elaborated by multivariate statistical analysis, (Principal Component Analysis, PCA).

GRAPHICAL ABSTRACT

Metal complexation capacity of Antarctic lacustrine sediments
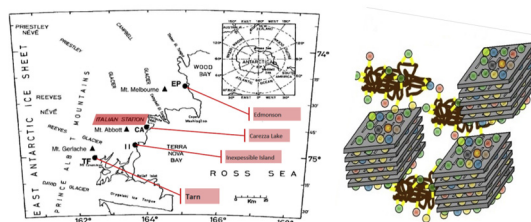
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ABSTRACT

The purpose of this study is to implement a work that is a part of a project funded by the Italian National Antarctic Research Program (PNRA, Piano Nazionale di Ricerche in Antartide) within the main thematic focus "Chemical Contamination-Global Change". This research was devoted to detect and characterize micro and nano components with strong complexing capability towards metal ions at trace level in sea water, lakes and lacustrine sediments, sampled during the XXII expedition of PNRA.

In particular, in the present work, the sorption complexation capacity of an Antarctic lacustrine sediments toward Cu(II) and Pb(II) is described. The characterization of the sorption was undertaken, studying kinetics and isotherm profiles. The lake here considered is Tarn Flat in the area of Terra Nova Bay. The sorption equilibria of Cu(II) and Pb(II) on the lacustrine sediments were reached in about 10 h, and they were best modelled by the Langmuir equation.

Preliminary, to establish if the data here obtained were consistent with those reported for the same area in other expeditions, a common multivariate techniques, namely the principal component analysis (PCA), was applied and finally the consistency of the data has been confirmed.

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1. Introduction

Antarctica is the only continent which is still partly unexplored. The geographical location and physical characteristics, as well as the distance from sources of pollution and an almost total absence of human disturbance, make it the largest and most unspoiled scientific laboratory of the world.

In the Victoria Land region a large number of lakes are present, and this scenario provides exceptional opportunities for studying biogeochemical processes in closed and fairly pristine lacustrine ecosystems. Nevertheless waters, soils and sediments from the Antarctic northern Victoria Land region (East Antarctica) have

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received little attention. Some studies, within the framework of the Italian National Antarctic Research Program (PNRA), reported the distribution of major, minor and trace elements in the ice, soils, sea waters, marine and costal sediments at Terra Nova Bay (Western Ross Sea) (Gragnani and Torcini, 1992; Ianni et al., 2010; Grotti et al., 2001, 2008). In these papers, the information on total metal ions content and in few cases the speciation pattern for trace elements were described.

Otherwise, few investigations were devoted to lacustrine sediments. Depth mineralogical and chemical characterizations of sediments in Antarctic lakes should be of interest for understanding geochemical and environmental processes and their possible variations maybe due to local anthropogenic activities, global contamination or climate changes (Gragnani and Torcini, 1992; Abollino et al., 2004; Malandrino et al., 2009; Libera and laghi).

In Terra Nova Bay the lakes are concentrated in zones with distinctive features that can be divided into five main areas: Edmonson Point, Northern Fotthills, Andersson Ridge, Inexpressible Island and Tarn Flat. The latter is the territory southernmost at about 60 km from the Italian base, and it is the largest ice-free area. The choice of sampling in the Tarn flat lake has been made since it is located in a catchment area of easy detection and it is fed, during the hottest summers, from melting waters of a small glacier (Mt. Gerlache) and/or other surface waters coming from the southern part of the basin and derived from the melting of permafrost or small snowfields. The lake is approximately 35 km from the sea, and it has a surface of around $18,000 \, m^2$ with a maximum depth of 3.9 m (Abollino et al., 2004; Malandrino et al., 2009).

The Tarn Flat lacustrine sediments are characterized by a large percentage of silt and clay, and this is due to the large size of the lake which allow the accumulation of thinner material on the lake bottom. Furthermore, the sediments contain calcite, fluorite and have a low level of marine origin salts, due to the fact that Tarn Flat lake is far from the sea (Malandrino et al., 2009; Libera and laghi). A detailed physicochemical characterization of the sediments, i.e. carbon/organic matter content, ash content, data on mineral phases, particle size, was previously reported by other authors and can be found, for instance, in reference (Malandrino et al., 2009).

In the present work the interpretation of the sorption capacity of the lacustrine sediments of Tarn flat lake, toward Cu(II) and Pb(II), was carried out through loading curves that can be interpreted as isothermal adsorption or ligand titration. The best fit for the two cations was obtained by applying the Langmuir equation, consequently it was possible to get both the constant K_L and the maximum sorption capacity q_{max}. For these experiments, it should be proved to be under thermodynamic conditions. Therefore, the kinetics of exchange have to be studied, with the aim of finding the time needed to reach equilibrium between solution and solid phases.

Preliminary, to check the consistency of our data with the historical ones, a common multivariate techniques, namely the principal component analysis (PCA), was applied. As historical records employed to establish the trueness of the metal ions analysis, we referred to the data base of PNRA (Anon).

2. Experimental

2.1. Samples

The lacustrine sediments sampling was carried out in January 16, 2007, during the XXII PNRA campaign. The site, where the sediments were collected, is located in Tarn Flat Lake (lake number 20, area SS5860, site 12, coordinates: 74° 58.173′ S, 162° 30.737′ E). Fig. 1 shows the specific point where sampling took place.
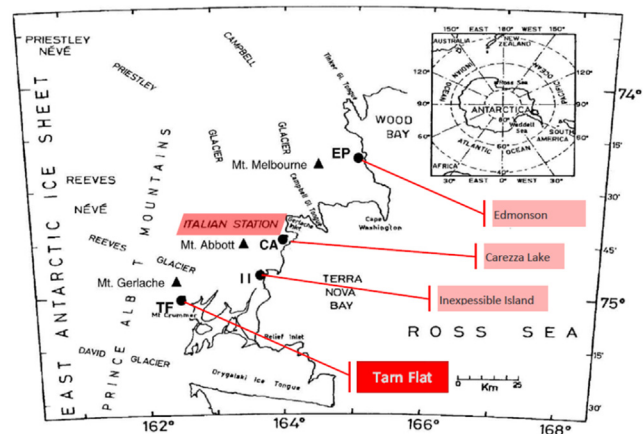

Fig. 1. Sampling site of lacustrine sediments in Tarn Flat Lake.

The lacustrine sediments of Tarn Flat were sampled to a depth of 20 cm from the surface of the lake through the use of a pallet scoop. Then they were put in a polyethylene container, bagged and carried in the chemical laboratories of the Antarctica Italian base. Here the samples were frozen and prepared for the further transport. In the summer of 2007, the cargo ship arrived in Italy; the samples were delivered in refrigerated trucks to the various University Research Units participating to the XXII PNRA campaign. A freezer at −30 °C, dedicated exclusively for this purpose, has preserved the samples delivered to the Pavia Unit during these years.

2.2. Reagents

All reagent were commercially available and used as received, unless otherwise indicated. All solutions were prepared using ultrapure MilliQ water (obtained by Simplicity185 apparatus, Millipore©).

HNO$_3$ ultrapure 65% (Fluka, CAS n° 7697-37-2); HF ultrapure 50% (Carlo Erba, CAS n° 7664-39-3); H$_2$O$_2$ 30% (w/w) in H$_2$O (Fluka, CAS n° 7722-84-1); KNO$_3$ 99.999 trace metal basis (Sigma Aldrich CAS n° 7757-79-1); 2-(N-morpholino) ethanesulfonic acid (MES) 99.5% (Sigma Aldrich, CAS n° 44-32-31-9) metal ions standard for AAS, TraceCERT®, 1000 mg L^{-1} in nitric acid (Sigma Aldrich).

2.3. Instrumentation and procedures

Handling of sediment samples was performed in a clean environment under a laminar flow hood.

Before the analysis, sediments were unfrozen overnight until reaching room temperature, dried at 70 °C for 2 h, powdered with a mortar of porcelain, and sieved through 1000 μm mesh sieve.

Only the fractions with particles smaller than 1 mm was used for all analyses.

2.3.1. Determination of the total metal ions content

Lacustrine sediment samples (0.25 g of dry and sieved material) were submitted to acid mineralization in a Parr acid digestion bomb with Teflon liner, with a mixture of concentrated HNO$_3$/HF/H$_2$O$_2$ (3 mL HNO$_3$ + 1 mL HF + 1 mL H$_2$O$_2$) at 140 °C overnight. After cooling at room temperature, the residual was diluted to 25 mL with MilliQ water; the total metal ions content in this solution was determined by ICP-OES analysis (ICP-OES Optima 3300 D, Perkin Elmer, USA). The external calibration method was used for the determination of each cation. 10 independent blank solutions (MilliQ water acidified at pH 2 with ultrapure nitric acid) were