

Final project report

Project ID 2006/9.01
Title Studio e caratterizzazione di microcostituenti chimici con proprietà complessanti forti nell'ambiente marino dell'Antartide, in relazione al ciclo stagionale di formazione/scioglimento del pack-ice

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Activities and results

The project was devoted to detect and characterize micro and nano components with strong complexing capability towards metal ions in some Antarctic waters. Such substances, even if present at very low concentration, are of overwhelming importance for the fate of heavy metals at similar concentration level, i.e. at micro/nano molar concentration. They are unquestionably more relevant than, for example, any inorganic ligands present at higher concentration, but usually exhibiting rather low complexation constant towards metals. Nevertheless, these ligands have been scarcely studied, particularly in the Antarctic environment, due to the difficulties connected to investigations of poorly defined substances at extremely low concentration. Strong metal ligands include an extremely large variety of substances. Natural organic matter of low and high molecular mass, produced by the activity of biota and by the degradation of vegetal tissues, are some of the candidate ligands. Often identified with humic or fulvic substances, they present a very complex molecular structure with a continuum of binding sites of different strength. Also synthetic chemicals could be present at sub-trace level, for example ethylenediamine tetracetic acid (EDTA), found in coastal areas along oceans. Also some inorganic compounds mainly high molecular mass metal oxides could give stable combination with metals.

This research project was mainly devoted to the investigation of strong ligands at low concentration in Antarctic waters of different salinity. The samples examined were collected during the 2006/2007 campaign in Antarctica, to which the members of this project were not allowed to participate. The samples were a sea water from Ross Sea (Gerlach Inlet, lat. 74°39'020" S, long. 164°07'020" E), and two natural waters of much lower salinity, obtained from two lakes, Tarn Flat (N. 20) and Edmonson Point (N.15), with well different characteristics as here reported:

	Coordinates	Altitude, m, a.s.l.	Distance from the sea, km	Depth, m	Kind of soil
Tarn Flat (N. 20)	74°59'S;162°33'E	-70	35	~ 3.9	Granitic soil
Edmonson Point (N. 15)	74°19'S;165°04'E	0	~ 0.5	~ 4	Quaternary, basaltic volcanic soil

The two lakes are frozen during the winter, completely ice-free during the Antarctic summer. They do not have defined inflow and outflow channels, their only input being from snow and ice melt.

The major ionic components of these samples are reported in Table 1.

Edmonson Point and Tarn Flat sites have been characterized in previous expeditions, but not for the complexing properties of water. Together with the water samples, sediments of the lakes were obtained.

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Table 1- Major ionic components of the Antarctic samples.

Ion	Lake EP (mg/l)	Lake TF (mg/l)	Ross Sea (mg/l)
Na ⁺	6.1(3)	24(1)	6243(338)
K ⁺	0.84(4)	1.9(2)	375(20)
Ca ²⁺	1.09(3)	6.3(2)	515(14)
Mg ²⁺	0.84(4)	2.22(3)	1048(15)
Cl ⁻	9.8(2)	67(2)	12091(1032)
SO ₄ ²⁻	2.1(6)	23(3)	249(29)
NO ₃ ⁻	0.6(4)	9.8(5)	17(5)
I (M)	5.86 10 ⁻⁴	3.50 10 ⁻³	0.545
pH ^a	8.16	8.20	

^a pH measured after defrosting at 25 °C.

Unfortunately only a few samples could be studied, because of the limitations of the Antarctic campaign of the year 2006-2007. Moreover all these samples were not temporarily differentiated, having been taken in the same period of the Antarctic summer.

In the present investigation, two approaches have been used to detect and characterize the complexing substances present at low concentration in the water phases. In the first one, the complexing substances have been detected by titration with copper(II), applying two monitoring methods with different detection window. The measurements were made respectively by electrochemical (cathodic stripping voltammetry) and spectrophotometric (atomic adsorption and emission) methods. These methods have low detection limits, which is the reason why they are convenient for the detection of ligands at very low concentration. The concentration of the copper(II) ligands and the stability constants of the complexes can be determined, but not the chemical nature of the ligand, even if the stability constant can give indirect indication.

In the second method the organic substances, not of humic/fulvic nature, with strong complexing properties towards metal ions have been investigated directly, after separation and information about the chemical nature of the strong ligands are obtained. Due to their very low concentration in the water phase, the investigation was dedicated to identify such substances in contiguous compartments, i.e. the sediments. Particularly phytochelatin, porphyrins and carotenoids were considered as possible metal ion complexing substances.

Identification of the strong copper(II) ligands in the Antarctic waters

The activity of two Research Units (Pavia and Insubria University) was specifically dedicated to the detection of the strong ligands in the water samples listed above by titration with copper(II). The two methods were competing ligand equilibration-cathodic stripping voltammetry (CLE-CSV) and resin titration (RT), with detection window respectively at around $\log \alpha = 4$ and $\log \alpha = 12-18$ (depending on the ionic composition of the sample). The side reaction coefficient of the metal ion, i.e. the ratio of total to free metal ion concentration is indicated by α . The interesting point is that information about ligands of different strength are obtained by the two methods, as reported in the Table 2.

One of the techniques, CLT-CSV (competing ligand titration), is a titration of the ligand in which the titrant, i.e. copper(II), is added to the sample and distributes between the natural ligand and an analytical ligand purposely added to the sample. In this form it is adsorbed at the working electrode and determined electrochemically by cathodic stripping voltammetry.

Table 2.
Results obtained by CLE-CSV with copper(II) (salicylaldoxime as analytical competing ligand. DW: $\log \alpha = 4$) (Monticelli et al., (2010), *Anal. Chim. Acta*, **675, 116)**

	c_l (M)	K'	Log α
Edmonson Point	4.6 10 ⁻⁹	2.4 10 ¹²	3.84
Tarn Flat	3.6 10 ⁻⁹	1.1 10 ¹³	1.88*
Ross Sea	4.9 10 ⁻⁹	6.9 10 ¹⁴	4.46

* α outside the detection window

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Results obtained by RT with copper(II) (iminodiacetic resin as sorbing solid. DW: $\log \alpha = 12-18$) (Thesis of A. Torchia, tutor G. Alberti, 2008-09)

	c_i (M)	K^*	$\log \alpha$	$\log I^*$
Edmonson Point	$1.0 \cdot 10^{-8}$	$4.5 \cdot 10^{23}$	15.3	-3.23
Tarn Flat	$6.4 \cdot 10^{-9}$	$2.4 \cdot 10^{20}$	12.1	-2.45
Ross Sea	$2.0 \cdot 10^{-9}$	$8.7 \cdot 10^{18}$	9.8	-0.26

*) I : ionic strength of the sample.

The second method, indicated as RT (resin titration), is a titration too, but the metal ion is subtracted from the sample, instead of being added, by competitive adsorption on a solid. This is obtained by equilibrating a sample volume V with g grams of solid at different values of the ratio V/g . The sorbing solid is a resin with completely known sorbing properties (Alberti, G., Biesuz, R. (2011) *React. Func Polym.*,71, 588), so that prediction at different conditions are possible. The amount of sorbed metal is determined after equilibrium conditions are reached. RT has been applied to several metal ions simultaneously, one of these metals being copper(II). A comparison of the results for different metal ions is reported in Table 3.

Table 3.
Simultaneous Resin Titration, RT of the Antarctic water samples.

<i>Sample: Lake Edmonson Point N. 15</i>				
$V = 100$ ml, $w = 0.07 \div 0.70$ g di membrana secca in forma NH_4^+				
	α	K^*^a	$c_{\text{tot,RT}}$ (M)	c_{tot} (M) ^b
Cd(II)	$< 2.0 \cdot 10^7$	$5.3 \cdot 10^{10}$	$1.4(5) \cdot 10^{-10}$	$1.1(1) \cdot 10^{-10}$
Cu(II)	$1.3(1) \cdot 10^{15}$	$7.4 \cdot 10^{17}$	$1.04(5) \cdot 10^{-8}$	$1.05(5) \cdot 10^{-8}$
Pb(II)	$< 1.2 \cdot 10^8$	$3.2 \cdot 10^{11}$	$1.2(3) \cdot 10^{-9}$	$1.0(1) \cdot 10^{-9}$
Zn(II)	$2.5(1) \cdot 10^7$	$1.9 \cdot 10^{10}$	$1.70(8) \cdot 10^{-8}$	$1.6(2) \cdot 10^{-8}$
pH = 7.12 after equilibration with the solid phase (Empore TM membrane)				

<i>Sample: Lake Tarn Flat N.20</i>				
$V = 100$ ml, $g = 0.07 \div 0.70$ g of solid phase (Empore TM membrane)				
	α	K^*^a	$c_{\text{tot,RT}}$ (M)	c_{tot} (M) ^b
Cd(II)	$7.0(3) \cdot 10^7$	$1.1 \cdot 10^{11}$	$1.1(1) \cdot 10^{-10}$	$8.3(4) \cdot 10^{-11}$
Cu(II)	$9.4(5) \cdot 10^{11}$	$5.4 \cdot 10^{14}$	$7.0(8) \cdot 10^{-9}$	$7.0(3) \cdot 10^{-9}$
Pb(II)	$< 6.5 \cdot 10^7$	$2.0 \cdot 10^{11}$	$3.6(1) \cdot 10^{-10}$	$3.3(2) \cdot 10^{-10}$
Zn(II)	$< 1.4 \cdot 10^7$	$4.3 \cdot 10^{10}$	$2.3(4) \cdot 10^{-8}$	$3.5(5) \cdot 10^{-8}$
pH = 7.33 after equilibration with the solid phase (Empore TM membrane)				

<i>Sample: Ross Sea</i>				
$V = 100$ ml, $w = 0.07 \div 0.70$ g di membrana secca in forma NH_4^+				
	α	K^*^a	$c_{\text{tot,RT}}$ (M)	c_{tot} (M) ^b
Cd(II)	$< 8.9 \cdot 10^4$	$2.4 \cdot 10^8$	$2.9(5) \cdot 10^{-10}$	$2.1(2) \cdot 10^{-10}$
Cu(II)	$3.0(2) \cdot 10^9$	$2.8 \cdot 10^{12}$	$1.6(2) \cdot 10^{-8}$	not determined
Pb(II)	$< 1.9 \cdot 10^4$	$4.0 \cdot 10^7$	$1.4(2) \cdot 10^{-10}$	$1.5(2) \cdot 10^{-10}$
Zn(II)	$< 4.6 \cdot 10^7$	$1.2 \cdot 10^7$	$2.9(2) \cdot 10^{-8}$	$2.9(3) \cdot 10^{-8}$
pH = 6.72 after equilibration with the solid phase (Empore TM membrane)				

^a K^* partition coefficient of the solid phase computed at the mean pH of the subsamples and at the ionic strength of the solution.;

^b Total metal concentration determined on a acidified portion of the original sample

The DW of RT is the side reaction coefficient of the sorption reaction, i.e. the ratio of the total adsorbed metal concentration in the resin to the free metal concentration in solution (K^*). It depends on the nature of the adsorbing solid, and in the case of ion exchanging complexing resins can be evaluated at different conditions (acidity, ionic composition) on the basis of the Gibbs-Donnan model, from the known adsorbing properties (Alberti, G. et al., (2008). *Analytical Sciences* 24, 1605).

The copper(II) complexes detected by the method at higher detection window are very strong. The ligands could be either particular sites at very low concentration in humic/fulvic substances with a structure well suited to copper(II) complexation, or by completely different ligands with complexation constants similar for example to those of EDTA or other Chelons.

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Such strong ligands can be detected only with a method at very high detection window. Actually RT is the method with highest DW so far known, which allows to detect very strong complexes. These strong complexes are evidently present in all the Antarctic waters considered

It is important to highlight that RT makes possible to determine the total concentration of the metal ion in the sample, even if it is linked to very strong complexes, due to the high detection window of complexing resins. Only the complexations with side reaction coefficient (α) near to the detection window (two orders of magnitude around the main value of DW) can be accurately characterized in terms of concentration and stability constant by the method. Thus the ligands detected by RT are stronger than those detected by CLE-CSV because of the higher detection window. In a few cases the experimental side reaction coefficient of copper(II) was outside the detection range of the method, so that these results could be inaccurate.

From the data reported in Table 2 it is seen that in all the samples considered strong ligands of copper(II) are present, both those determined with CLE-CSV and the RT method. It must be stressed that the strong copper(II) ligands are present also in the lakes which are completely frozen during the Antarctic winter. Nevertheless a biological activity exists, as it has been demonstrated by the investigation on the sediment composition (Giovannetti, R. et al., 18th International Mass Spectrometry Conference, Bremen, Germany, 30 August - 4 September 2009).

The complexation constants determined by the RT method increase from $\log K=19$ to $\log K=24$ with decreasing ionic strength. This suggests that a competition could exist between copper(II) and other metal ions present in the samples, at concentration increasing with the ionic strength, as for example alkaline earth metal ions (see Table 1).

The trend observed in the case of weaker ligands, $\log K=12-14$, detected by CLE-CSV, is different, i.e. the stability constant of the complex with copper(II) increases at increasing ionic strength. This is not easily explainable in terms of ionic compositions of the considered samples, since the difference is too high to be justified by the ionic strength effect on the activity coefficients of small ions. However it could demonstrate an increasing charge shielding on positively charged ligands of micellar dimensions. It can not be excluded that different ligands are present in the three considered Antarctic waters, i.e. the two lakes and Ross Sea, with increasing stability constant with copper(II).

The experimental methods applied for the detection and thermodynamic characterization of the complexes and ligands in the Antarctic samples examined have been developed and characterized during the first part of the research, from the treatment of the sample, included the mineralization of the organic substance (Monticelli D. et al., (2010) for *Microchemical Journal*, 95 158), to the evaluation of the analytical performances of the methods (Alberti, G. et al, (2007) *Anal. Chim. Acta* 599, 41; Monticelli D. et al., (2010) *Anal. Chim. Acta*, 675, 116,), to the development of new sorbing materials more convenient for RT (Alberti, G., Biesuz, R. (2011) *React. Func. Polym.* 71 588).

It has been demonstrated that a complexing resins with very high DW can be used as a sensor for free metal ion concentration determination, at very low levels, as for example 10^{-18} M in the case of copper(II) (Pesavento, M. et al., (2008) *Solvent Extraction and Ion Exchange* 26, 301).

The sorbing properties of an iminodiacetic resin useful for RT at high DW at different temperatures, have been determined (Alberti, G. et al., XX Congresso Nazionale di Chimica Analitica, S. Martino al Cimino (Viterbo) 16 - 20 September 2007). The idea was to develop a RT procedure for application in Antarctica, with the aim to perform the detection of ligands directly in situ, so as to limit as much as possible the perturbation of the sample, in particular the frosting and defrosting, which could damage the ligand substances. Unfortunately the practical application was not possible, because of the limited time of the research. The application of the developed methods to similar natural matrices, and also to synthetic samples containing known ligands, for validation purposes, has been carried out. It is particularly interesting to notice that CLE-CSV and RT gave very similar results in the case of synthetic samples (Alberti, G. et al., *Progetto per la validazione del grado di complessazione dei metalli in acque ambientali XXI* Convegno nazionale della Divisione di Chimica Analitica della Società Chimica Italiana, Arcavacata di Rende (CS), 21 - 15th september 2008)

Extraction and separation from Antarctic samples of strong metal ligands

Two research Units (Camerino and Parma) were involved in the structural characterization of possible ligands of copper(II), and other metal ions, present in the Antarctic samples considered. It has been demonstrated by the titration methods described above that the strong ligands are present at very low concentration, i.e. nM level, in water phase, so that it is impossible to examine this phase directly. Instead contiguous compartment were considered, in particular the sediments.

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Organic components of the sediments different from humic/fulvic acids, were extracted and analyzed using reversed phase high performance liquid chromatography (HPLC) with electrospray-mass spectrometry (ESI-MS) detection and diode array detection (DAD).

Some results are reported in Table 4.

Table 4
Organic components of Edmonson Point lake sediments.

No	retention time (min)	λ max (nm)	ESI(+)	Pigment
1	5.13	385,460,610	547	Reduced Scytonemin
2	5.9	410, 540, 610, 665	610	Chlorophyll c1
3	7.8	410, 540, 610, 665	608	Chlorophyll c2
4	8.39	390	-	Chlorophyllide a
5	22.84	470, 605,650,695	906	chlorophyll b
6	23.14	405, 500, 535, 605, 665	871	Pheophytin a
7	24.35	380, 410,430, 615, 665	892	Chlorophyll a
8	24.59	(415)440, 600, 655	885	Pheophytin b
9	25.07	(405), 500, 535, 605, 665	-	Pheophytin a type
10	25.91	405, 500, 535, 605, 665	-	Pheophytin a type
11	26.15	405, 500, 535, 605, 665	-	Pheophytin a type
12	27.33	405, 500, 535, 605, 665	606	Phaeophorbide a

Organic components of Tarn Flat lake sediments.

No	retention time (min)	λ max (nm)	ESI(+)	Pigment
1	3.2	390	545	Scytonemin
2	3.67	390	-	Scytonemin type

The presence of these pigments is indicative of lake life under extreme environmental Antarctic conditions, despite of the fact that the lakes are frozen for a large part of the year, and of the life degradation in the lakes.

In particular there is not any evidence of chlorophyll dyes in the sediments of Tarn Flat, which can be explained considering that algae are scarcely degraded, and release a low amount of chlorophyll in the sediments. Instead, some dyes of the scytonemines family have been detected in Tarn Flat, demonstrating the presence of cyanobacteria colonies. This pigment is produced in response to elevated levels of UV-A radiation. Considering the chemical structure of scytonemines, they should not be strong copper(II) ligands.

Dyes of the chlorophyll family have been detected in Edmonson Point sediments. Substances of this kind could actually strongly complex metal ions, in particular copper(II). Stability constants with Cu(II) as high as $\log K=38$ have been determined in mixed solvents with porphyrinic ligands. This could parallel the previous observation (Table 2) that the concentration of strong ligands is somewhat higher in Edmonson Point than in Tarn Flat.

Other interesting compounds of natural origin with strong complexing properties for metal ions are phytochelatins, which are cystein-rich metal binding (poly)peptides synthesized in plants and in other organisms from glutathione (GSH) to counteract the toxic effects of heavy metal ions. In plants, the in vivo synthesis of PCs can be induced at different extents by a variety of metal ions, the most effective of which is cadmium, supporting the notion of a direct role of PCs in intracellular heavy metal sequestration and detoxification. S-Nitrosylation, i.e. the replacement of the hydrogen atom in the thiol group of cysteine (Cys) residues with a -NO moiety (SNO), has emerged as a key reaction in several metabolic processes occurring in animals and in plants. Methods for the identification and determination of phytochelatin and S-NO phytochelatin have been developed by the Parma Unit, in an attempt to identify substances of this kind in Antarctic samples (Elviri L. et al., (2010) *J. of Chromatography A*, 1217, 4120.). Preliminary investigation did not revealed significant levels of NO-phytochelatin in Antarctic plants neither in the sediments of the two considered lakes. This could parallel the low cadmium content (see Table 3).

Complexing properties of Antarctic sediments

The complexing properties of the sediments have been investigated by a dynamic method by the Pavia-Torino RU. Only preliminary results have been obtained, by flowing a synthetic copper(II) solution of known concentration (1.2 ppm in HEPES buffer at pH=6.5) through a column containing the sediment (column obtained with 0.5 g of dry sediment at controlled granulometry), and the copper(II) concentration in the eluate was determined. From the breakthrough curve of the considered metal ion it has been found that the

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capacity of the Tarn Flat sediment is lower than that of Edmonson Point sediment, which could confirm that the former sediment contains a lower amount of complexing organic matter.

Preliminary investigations about the adsorbing properties of the inorganic components in the absence and in the presence of organic ligands (oxalic acid and EDTA) have been carried out by the Torino Unit (Abollino, O. et al., (2008) *Applied Clay Science* 38, 227).

A summary of the results obtained by the different characterization methods of the samples from the three locations listed in Table 3 has been presented at the XXII Congresso Nazionale della Divisione di Chimica Analitica Società Chimica Italiana (Como, 12-16th September 2010).

Products

A – papers in scientific magazines

1. **Abollino, O., Giacomino, A. M. Malandrino, Mentasti E.** (2008) Interaction of metal ions with montmorillonite and vermiculite. *Applied Clay Science* **38**, 227–236
2. **Alberti, G., Biesuz, R.** (2011) EmporeTM membrane vs. Chelex 100: thermodynamic and kinetic studies on metals sorption, *React. Func Polym.* **71** 588-598
3. **Alberti, G., Biesuz, R., Huidobro, C., Companys, E., Puy, J., Galceran, J.** (2007). A comparison between the determination of free Pb(II) by two techniques: Absence of gradients and Nernstian equilibrium stripping and resin titration. *Analytica Chimica Acta* **599**, 41-50.
4. **Alberti, G., Biesuz, R., Pesavento, M.** (2007). Determination of the total concentration and speciation of Uranium in natural waters by the Resin Titration method. *Microchemical Journal* **86**, 166-173.
5. **Alberti, G., Biesuz, R., Pesavento, M.** (2008). Determination of the Total Concentration and Speciation of Metal Ions in River, Estuarine and Seawater Samples. *Analytical Sciences* **24**, 1605-1611.
6. **Biesuz, R., Alberti, G., D'Agostino, G., Magi, E., Pesavento, M.** (2006). Determination of cadmium(II), copper(II), manganese(II) and nickel(II) species in Antarctic seawater with complexing resins. *Marine Chemistry* **101**, 180-189.
7. **Giovannetti, R. Alibabaei, L. Pucciarelli, F.** (2008) Kinetic and photochemical behaviour of Zn(II)-Coproporphyrin-I complex: a spectrophotometric and fluorimetric study. Evidence of Sitting Atop complex formation, *Current Topics In Analytical Chemistry*, **7** 15-20.
8. **Giovannetti, R. Alibabaei, L. Pucciarelli, F.** (2009) Kinetic model for astaxanthin aggregation in water-methanol mixtures, *Spectrochimica Acta Part A* **73** 157–162.
9. **Giovannetti, R. Alibabaei, Petetta, L.** (2010) Aggregation behaviour of a tetracarboxylic porphyrin in aqueous solution, *Journal of Photochemistry and Photobiology A: Chemistry* **211** 108-114
10. **Giovannetti, R., Bartocci, V., Pucciarelli, F., Petetta, L.** (2008) Remarks on the reactions of a tetracarboxylic porphyrin with gold and silver ions: A spectrophotometric, TEM and SEM study, *Polyhedron*, **27** 1047-1053.
11. **Monticelli D., Carugati G., Castelletti A., Recchia S., Dossi C.** (2010) Design and development of a low cost, high performance UV digester prototype: application to the determination of trace elements by stripping voltammetry, *Microchemical Journal*, **95** 158 – 163
12. **Monticelli D., Dossi C., Castelletti A.,** (2010), Assessment of accuracy and precision in speciation analysis by competitive ligand equilibration–cathodic stripping voltammetry (CLE–CSV) and application to Antarctic samples, *Analytica Chimica Acta*, **675**, 116 – 124
13. **Pesavento, M., Biesuz, R., Alberti, G., Profumo, A., D'Agostino, G.** (2004). Speciation of copper(II) in natural waters in the presence of ligands of high and intermediate strength. *Chemical Speciation and Bioavailability* **16**, 35-43.
14. **Pesavento, M., Profumo, A., Biesuz, R., and Alberti, G.** (2008). Ion exchange complexing resins as sensors for the determination of free metal ion concentration at a low level. *Solvent Extraction and Ion Exchange* **26**, 301-320.

B – book chapters

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C - proceedings of international conferences

1. **Alberti, G., Biesuz, D'Agostino G., R. Pesavento M.,** *Fulvic acids as multimodal strong ligand for lead(II) in aqueous solutions* 41st IUPAC World Chemistry Congress Turin (Italy) August 5-11, 2007
2. **Alberti, G., Biesuz, R., Pesavento, M.** *Determination of the total concentration and speciation of metal ions in river, estuarine and sea water samples* 14th International Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region Sevilla (Spain) October 10-14, 2007
3. **Alberti, G., Pesavento M., Biesuz, R.** *Characterization of natural ligands of lead(II) at low concentration by using sorbing solids as sensors for free metal ion* XVIII Spanish-Italian Congress on the Thermodynamics of Metal Complexes S. Margherita di Pula (CA) (ITALY) June 5-9th 2007

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4. **Alberti, G., Pesavento M., Biesuz, R.** *Determination of the total concentration and speciation of uranium in natural waters by the resin titration method* XVIII Spanish-Italian Congress on the Thermodynamics of Metal Complexes S. Margherita di Pula (CA) (ITALY), June 5-9th 2007
5. **Castelletti, C. Dossi, D. Monticelli** *Assessment of accuracy and precision in speciation analysis by CLE–CSV: application to Antarctic samples* 12th Workshop on Progress in Analytical Methodologies for Trace Metal Speciation, Mainz (Germania), 15 – 18 settembre 2009
6. **Dossi, D. Monticelli, Castelletti, C.** *Accuracy and precision in speciation analysis: the case of Competitive Ligand Equilibration coupled to Cathodic Stripping Voltammetry detection of the labile fraction* 3rd EuChemS Chemistry Congress, Norimberga (Germania), 29 agosto – 2 settembre 2010
7. **Elviri L., Speroni F., De Michele R., Vurro E., Di Valentin M., Lo Schiavo F., Careri M., Mangia A.,** *Mass spectrometry studies of S-nitrosylated peptides in plant proteomics* HUPO 7th World Congress, 16-20 Agosto 2008, Amsterdam, Olanda
8. **Giovannetti, R. Alibabaei, L. Pucciarelli, F.** *ESI-MS studies of sedimentary pigments in reversed-phase HPLC system* 18th International Mass Spectrometry Conference, Bremen, Germany, 30 August - 4 September 2009
9. **Mucchino C., Elviri L., Mangia A., Maffini M.,** *IC-DAD-IC-MS: a further approach to metal speciation* Winter Conference on Plasma Spectrochemistry Fort Myers, Florida, January 3 - 9, 2010
10. **Pesavento M., Alberti, G., Biesuz, R., D'Agostino G.,** *Speciation investigation of trace metal ions using complexing resins as sensors for the free metal ion concentration in real samples* TraceSpec 2007-11th Workshop on Progress in Analytical Methodologies for Trace Metal Speciation Münster (Germany) September 4-7, 2007

D – proceedings of national meetings and conferences

1. **Alberti, G., Biesuz, R., Sturini M., Pesavento M.,** *Complexation of lead(II) at low concentration by the fulvic fraction of a marine sediment: effect of the heterogeneity of the fulvic matter.* VIII Congresso INCA "Chimica Sostenibile e tecnologie ambientali: stato dell'arte e prospettive" Bologna (Italia) 2006, March 23-24th
2. **Alberti, G., M.G. Guiso, Torrisi I., Biesuz, R.** *Caratterizzazione dell'adsorbimento del Fe(III) su una membrana chelante. Aspetti cinetici e termodinamici* XXI Convegno nazionale della Divisione di Chimica Analitica della Società Chimica Italiana, Arcavacata di Rende (CS), 21 – 15 settembre 2008
3. **Alberti, G., Pesavento M., Biesuz, R.** *Studio preliminare per un'indagine volta a valutare l'effetto sulla speciazione dei metalli pesanti in acque naturali campionate a temperatura molto diversa dalla convenzionale T=25 °C dei laboratori di analisi.* XX Congresso Nazionale di Chimica Analitica S. Martino al Cimino (Viterbo) 16 - 20 Settembre 2007
4. **Alberti, G., Pesavento M., Biesuz, R., Monticelli D., Dossi C.** *Progetto per la validazione del grado di complessazione dei metalli in acque ambientali* XXI Convegno nazionale della Divisione di Chimica Analitica della Società Chimica Italiana, Arcavacata di Rende (CS), 21 – 15 settembre 2008
5. **Alberti, G., Pesavento M., Biesuz, R.,** *Speciation of metal ions in natural waters sampled at temperature far from the conventional lab T of 25°C* XII Convegno Nazionale Chimica degli Ambienti Polari, Venezia 22 – 23 giugno 2009
6. **Castelletti A., Dossi, C., Monticelli D.** *Validazione dei protocolli di speciazione dei metalli in traccia e loro applicazione a campioni antartici* XXII Convegno nazionale della Divisione di Chimica Analitica della Società Chimica Italiana, Como, 12 – 16 settembre 2010
7. **Castelletti A., Monticelli D., Carugati G., Dossi C.** *Progettazione e validazione di un sistema di digestione UV ad alta efficienza per l'analisi di ioni metallici tramite tecniche voltammetriche* XXI Convegno nazionale della Divisione di Chimica Analitica della Società Chimica Italiana, Arcavacata di Rende (CS), 21 – 15 settembre 2008
8. **Dossi, C. Castelletti, A. Pozzi A., Monticelli D.** *Assessment of accuracy and precision in speciation analysis by Competitive Ligand Equilibration with Cathodic Stripping Voltammetric detection* XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA) 5 – 10 luglio 2009
9. **Monticelli D., Castelletti A., Dossi, C., Alberti G., Pesavento M., Biesuz R.** *Specie complessanti forti nelle acque marine antartiche: confronto tra metodi analitici con competizione dei leganti* XXII Convegno nazionale della Divisione di Chimica Analitica della Società Chimica Italiana, Como, 12 – 16 settembre 2010
10. **Monticelli D., Castelletti A., Pozzi A., Dossi C.** *Validazione dei protocolli di speciazione dei metalli in traccia e loro applicazione a campioni antartici* XII Convegno Nazionale Chimica degli Ambienti Polari, Venezia 22 – 23 giugno 2009
11. **Speroni F., Terenghi M., Elviri L., De Michele R., Vurro E., Lo Schiavo F., Careri M., Mangia A.,** *Caratterizzazione diretta di fitochelatine nitrosilate in cellule di Arabidopsis thaliana trattate con cadmio mediante LC-ESI-LIT-MS/MS e LC-ESI-QTOF-MS* XXI Congresso Nazionale di Chimica Analitica, 21-25 Settembre 2008, Arcavacata di Rende (CS), Italia

E – thematic maps

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F – patents, prototypes and data bases

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G – exhibits, organization of conferences, editing and similar

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H - formation (PhD thesis, research fellowships, etc.)

1. **Assegno di ricerca:** "Messa a punto di metodiche analitiche per l'analisi e la speciazione di metalli in tracce all'interfaccia acqua di mare/pack su campioni prelevati presso la stazione italiana in Antartide" Assegnista: Dott. Alessio Castelletti, Responsabile scientifico: Prof. Carlo Dossi 1 marzo 2008 – 31 agosto 2008
2. **Assegno di ricerca:** "Caratterizzazione di microcostituenti chimici con proprietà complessanti forti nelle acque naturali" Assegnista: Dott. Alessio Castelletti, Responsabile scientifico: dott. Damiano Monticelli 1 marzo 2009 – 28 febbraio 2010

thesis

1. **Tesi Sperimentale di Laurea in Chimica dell'Ambiente di Stefano Marè:** *Extraction and identification of sedimentary pigments in Antarctic lakes of Edmonson Point and Tarn Flat.* relatore Rita Giovannetti, A.A. 2007-2008.
2. **Tesi di laurea magistrale in Chimica di Laura Albertario:** *Studio preliminare per indagini ambientali su acque naturali a bassa temperatura attraverso l'impiego di una resina chelante,* Relatore: Antonella Profumo; Correlatore: Raffaella Biesuz, A.A. 2007/08.
3. **Tesi di Laurea in Chimica di Laura Buglioni** *Determinazione degli elementi nei sedimenti dei laghi antartici presenti a Edmonson Point e Tarn Flat tramite la tecnica ICP-MS,* Relatori Stefano Ferraro, Rita Giovannetti, A.A. 2007-2008
4. **Tesi sperimentale della laurea Specialistica in Chimica di Antonio Torchia** "Determinazione della distribuzione di specie metalliche in tracce in campioni antartici" relatore Giancarla Alberti aa 2008-09
5. **Tesi di Laurea Specialistica in Chimica di Matteo Ottini**
6. "Caratterizzazione degli equilibri di adsorbimento di ioni metallici su membrana Empore™ a diverse temperature" relatore Giancarla Alberti aa 2008-09

Research units

Research unit 1 –PAVIA

Raffaella Biesuz	Ricercatore	UNIPV
Maria Pesavento	Professore Ordinario	UNIPV
Ornella Abollino	Professore Associato	UNITO
Antonella Profumo	Professore Ordinario	UNIPV
Giancarla Alberti	Ricercatore	UNIPV
Michela Sturini	Ricercatore	UNIPV
Girolamo D' Agostino	Dottorando	UNIPV
Daniele Merli	Assegnista	UNIPV
Lucia Cucca	Tecnico	

Research unit 2 –COMO

Carlo Dossi	Professore Ordinario	UNINSUBRIA
Andrea Pozzi	Professore Associato	UNINSUBRIA
Sandro Recchia	Professore Associato	UNINSUBRIA
Damiano Monticelli	Ricercatore	UNINSUBRIA
Laura Rampazzi	Ricercatore	UNINSUBRIA
Barbara Giussani	Ricercatore	UNINSUBRIA
Andrea Credaro	Dottorando	UNINSUBRIA
Elena Ciceri	Dottorando	UNINSUBRIA

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Research unit 3 Parma

Mangia Alessandro	Professore ordinario	UNIPR
Claudio Mucchino	Professore Associato	UNIPR
Lisa Elviri	Ricercatore	UNIPR
Diego Beltramii	Dottorando	UNIPR
Monica Maffini	Contrattista	UNIPR
Marinella Chierici	Tecnico	UNIPR

Research unit 4 Camerino

Paolo Passamonti	Ricercatore	UNICAM
Filippo Pucciarelli	Professore ordinario	UNICAM
Rita Giovannetti	Ricercatore	UNICAM
Stefano Ferraro	Ricercatore	UNICAM
Omar Bartomeoli	contrattista	UNICAM

Pucciarelli and Bartomeoli retired at the end of the first year

Date:

Notes