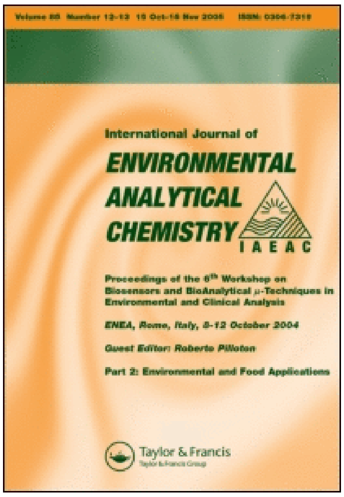

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A Voltammetric Study on Toxic Metals, their Speciation and Interaction with Nutrients and Organic Ligand in a South Pacific Ocean Region

H. Ida de Gregori[a]; D. Diana Delgado[a]; C. Hugo Pinochet[a]
[a] Chemical Institute, Catholic University of Valparaiso, Valparaiso, Chile

To cite this Article de Gregori, H. Ida , Delgado, D. Diana and Pinochet, C. Hugo(1988) 'A Voltammetric Study on Toxic Metals, their Speciation and Interaction with Nutrients and Organic Ligand in a South Pacific Ocean Region', International Journal of Environmental Analytical Chemistry, 34: 4, 315 — 331

To link to this Article: DOI: 10.1080/03067319808026847

URL: http://dx.doi.org/10.1080/03067319808026847

Int. J. Environ. Anal. Chem., Vol. 34, pp. 315–331
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Great Britain

A Voltammetric Study on Toxic Metals, their Speciation and Interaction with Nutrients and Organic Ligand in a South Pacific Ocean Region

IDA DE GREGORI H., DIANA DELGADO D. and
HUGO PINOCHET C.

Chemical Institute, Catholic University of Valparaiso. P.O. Box 4059, Valparaiso, Chile

(*Received* 9 *May* 1988; *in final form* 16 *June* 1988)

Dissolved cadmium, copper and lead present as labile complexes and non-labile complexes with organic ligand evaluated by anodic stripping voltammetry at natural pH and pH 2, with and without UV radiation, in surface sea water in the Valparaiso Bay. The vertical profiles of these trace metals levels and the phosphate, nitrate and dissolved oxygen were also determined for samples collected in the ocean at 22 miles off the coast. The cadmium profiles resemble those of nitrate more than those of phosphate and dissolved oxygen. Better correlation for plotted metal concentration versus nutrients concentration was established for cadmium nitrates.

The complexation capacity of coast natural seat water was studied for Cu^{+2} in samples which have not been subjected to any pretreatment except the 0.45 μm filtration. In order to obtain information about heavy metal biodisponsibility in presence of anthropogenic organic ligand (nitrilotriacetic acid) the stability constant for Pb(II)-NTA complex was determinated in the same sea water samples, at natural pH.

KEY WORDS: Surface sea water, cadmium, copper, lead, anodic stripping voltammetry, vertical profiles.

INTRODUCTION

The systematic application of voltammetry in all branches of aquatic trace metal chemistry has yielded, in recent years, a substantial amount of reliable data and extended greatly the knowledge on the levels, fate and behaviour of important toxic trace metals in the oceans coastal water and generally in the aquatic environment. Dissolved trace metals exert divers toxic effects, depending on their chemical form, on different types of organisms perturbing the ecosystems.[1-6]

As consequence of increasing emissions from anthrophogenic sources (metal ore mining, processing and usage of metals fossil fuel burning, fungicides, fertilizers, municipal wastes sewage) the general abundance of toxic metals in certain parts of the world has reached intolerable and hazardous levels. Special feature of toxic metals is that they are not biodegradable and have a pronounced tendency to be accumulated in vital organs. Thus, once they have entered the environment, their potential toxicity is controlled to a large extent by their physicochemical form.

Within the biogeochemical cycle, the sea has the important function to act as pseudo-sink with continuous inputs by rivers, continental run off and via the atmosphere in the form of wet and dry deposition. Particularly vulnerable to toxic metal pollution are the coastal zones and estuaries; they are the areas from which a substantial part of marine food originates and where a future improved sea food production by large scale aqua culture and fish farming is to take place. Therefore the reliable determination of the overall concentrations of dissolved toxic trace metals is an important task in the research on base line distribution and in surveillance on heavy metal pollution of the marine environment. In this context the speciation of dissolved heavy metals as function of the basic parameters of natural waters (salinity, pH, oxygen levels, nutrients concentration, depth and composition of dissolved organic materials) has a great significance. The dissolved state is the predominant phase of exchange, uptake and release by suspended particulates, sediments and aquatic organisms at various trophic levels.[1-7,8]

This is a very important research field for which the voltammetric approach, due to its inherent properties and well recognized potentialities, has gained a prominent position in recent years.[1,7,9-20] Although a great number of research on the concentration distribution and speciation of heavy metals in sea water have been carried out on several oceans, little information are available for the South Pacific Ocean, specially the region surrounded the large coastal areas of Chile, a country with high production of sea foods.[21]

This paper reports a voltammetric study on the concentration levels and speciation of dissolved lead, copper and cadmium in sea water samples taken from Valparaíso Bay (Chile). Their correlation with phosphates and nitrates and dissolved oxygen are also considered.

The investigation was extended to determine the complexation capacity of sea water for Cu(II) and to evaluate, in this medium, the conditional constant K′ of Pb (II)–NTA (nitriio-triaceticacid), a chelator that has not only model character but may also occur as pollutant in natural waters.[7,22–31] These are only some of the parameters of a natural water which are conveniently determined by voltametric techniques.[1,9,11,13,16,20,25–38]

EXPERIMENTAL

Sampling and treatment

The respective sampling procedure depends on the region where the samples were collected and the analysis to be undertaken. All sampling flasks and materials were acid cleaned, rinsed with Milli Q water and stored inside polyethylene bags up to the moment of sampling.

For heavy metals determination and speciation the sea water samples were collected manually on coastal areas at about 50 cm below the water line, with polyethylene flasks at several stations in the Valparaíso Bay, from May 1981 to June 1983 (Fig. 1). This Bay is surrounded by Valparaíso and Viña del Mar cities and receives the Aconcagua river and industrial and domestic wastes.

Sample were pressure filtered through 0.45 μm membrane filters. The membrane and the filter system were subjected, before use, to a scrupulous cleaning procedure and were conditioned with the same water sample. In this natural pH filtrate, the concentration of labile heavy metal was determinated. Subsequently an aliquot of filtrate was acidified with concentrated HCl (suprapure Merck) to pH 2 and another aliquot was subjected to UV irradiation in a closed quartz flask to release the trace metals bound to organic matter.[1,2,4,5,11,16,29,30,39–41] The non-labile species were decomposed by photolysis. 100 ml of sample was picked up with 100 μl of H_2O_2(30 %) and was irradiated overnight with a UV light from a 150 W mercury arc lamp.[1,41]

Determination of heavy metals was performed in the sample acidified

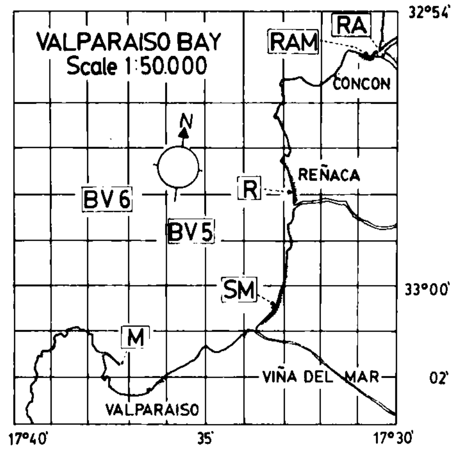

Figure 1 Map showing stations of sea water sampling at Valparaíso Bay, Chile.

to pH 2 or pretreated by irradiation. If the analysis was not carried out immediately, the filtered samples were stored at −20°C until they were analysed.

The samples from deeper waters, used to obtain the vertical profiles of trace metals and nutrients, were collected 22 miles of the coast (32°45′ S, 72°00′ W) during three different Valparaíso Cruises (August, October and December 1982), financed by the National Oceanographic. Committee. Samples were collected with precleaned Niskin sampler. For heavy metals determination an aliquot was transferred into a polyethylene flask and immediately acidified to pH 2 with HCl and then stored at −20°C. These samples were not filtered because the amount of suspended particulate matter was negligible and the contamination risk in the ship had to be minimized. The aliquot for nutrient determination was preserved by addition of $CHCl_3$ and stored in dark at 4°C at natural pH.

Complexation capacity and conditional constant determination were carried out immediately after sampling using water samples collected manually in coastal areas which had not been subjected to any pretreatment than filtration.

Voltammetric determination of heavy metals

The determination of heavy metals was carried out by anodic stripping voltammetry (ASV) or by differential pulse anodic stripping voltammetry (DPASV) at mercury film electrode, formed *in situ*, on a glassy carbon electrode with either a Tacussel electrochemistry system or with a Ladem pulse polarograph (made in the electronic laboratory of Catholic University of Valparaíso, Chile). A 25 ml of sample was placed in the electrolysis cell (with three electrodes system), the solution was spiked with 200 μl of Hg^{+2} (1.0 gl^{-1}), and then deaereated with purified nitrogen. During the cathodic deposition stage the potential electrode was kept at -1.0 V (SCE) with the electrode rotating at 2500 rpm during variable times, depending on the concentration of heavy metals. Then the rotation was stopped and a quiescent period of 30 s followed. The stripping voltammogram was then obtained in the quiet solution by ASV or DPASV while the potential was scanned to -0.1 V.

In the differential pulse mode the parameters were: pulse height 50 mV, pulse repetition time 0.2 s, pulse duration time 20 ms and scan rate 5 mV s^{-1}. After oxidation, the electrode was rotated and the potential held at -0.1 V for 3 min. The metals concentration was evaluated by standard addition with decreasing deposition time. The mercury film was removed when a new aliquot was going to be analysed.

Complexation capacity was evaluated using a hanging mercury drop electrode. Cathodic deposition of unchelated copper (II) was performed at -0.9 V and the DPSAV peak was recorded after successive addition of Cu^{+2}.

The conditional stability constant K′ was determined with a mercury film electrode previously obtained in other electrochemical cell, containing 2×10^{-5} M Hg^{+2} in 0.5 M KCl. For this experiment, the sea water sample was spiked with 2×10^{-8} M Pb^{+2} and the corresponding reversible DPASV response of unchelated Pb(II) was recorded. Subsequently, increasing concentration of the chelating ligand NTA were added and the corresponding decreasing peak of labile Pb was recorded, after an equilibration period of 30 min. This time had been determined in a preliminary study on the kinetics of complex (Pb(II)-NTA formation in sea water, which showed that equilibrium was attained with this time.

Nutrient and dissolved oxygen determination

Nutrients were determined spectrophotometrically using an autoanalyser LADEM ECMA (built in the Catholic University, Valparaíso). Phosphate determination was realized by phosphomolydate complex formation using hydrazine as reducing agent.[44] Nitrates were previously reduced to nitrites in a copperized cadmium column and then treated with sulfanilamide and n-naphtylamine.[45] The measurements were made at 885 nm and 543 nm respectively in a 5.0 cm path length cell. Dissolved oxygen was analyzed using the Carpenter modification to the Winkler method.[46]

RESULTS AND DISCUSSION

Conditions for the electrochemical determination were studied in order to improve the sensitivity and reproducibility of the method. The dependance of the peak current (ip) on the electrode deposition time (td), metal concentration, scan rate (v), electrolytic deposition potential (Ep), rotation speed of the electrode, the pulse height and amplitude, and pulse repetition time were studied in order to corroborate first the theoretical relations for ASV and DPASV and then to choose the experimental conditions for sea water analysis.

The general analytical procedure for sea water samples is summarized in Fig. 2 and was applied in samples collected in Valparaíso bay. The dissolved heavy metal concentration determinated at natural pH in the sea water sample represents the labile complex species and hydrated cations. This species yields, on ASV or DPASV, a common reversible response. When additional amount of a heavy metal is determined after acidification to pH 2, it corresponds to the fraction which is released from complexes with the dissolved organic matter (DOM) components or from colloids by exchange processes with H_3O^+ ions.[1,4,11,16,29,30,43] The results obtained are shown in Table I and are in accordance with this postulate. Samples taken at SM station where higher concentration differences are observed reflect the effect of municipal waste discharge.

When the acidified filtrate is subjected to UV irradiation, dissolved organic matter is decomposed by photolysis and the heavy metals released can be determinated as labile complexes. The results of the third column of Table I show that in general these values are higher than those

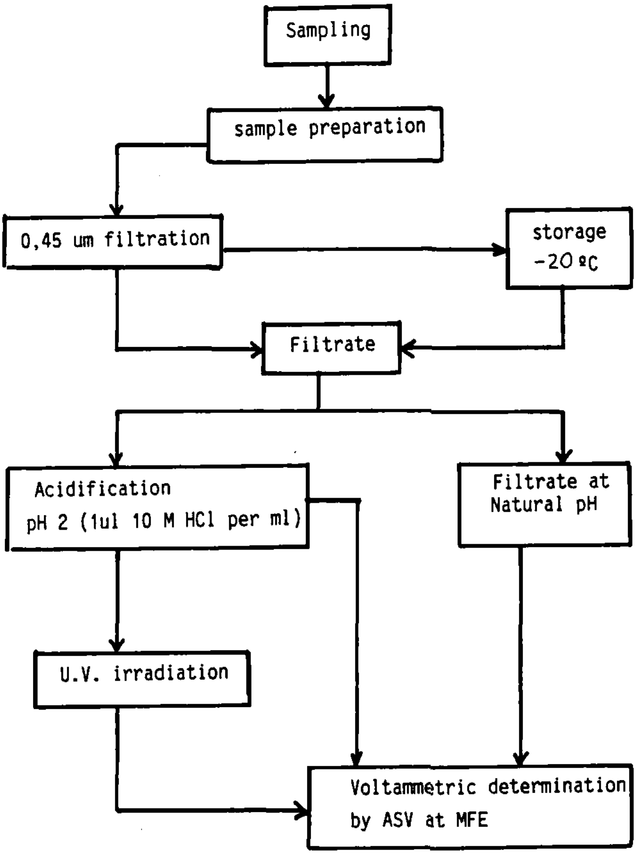

Figure 2 General analytical procedure for sea water samples analysis.

reported at natural pH and pH 2, particularly for Cu(II) and Pb(II) in SM station. These results are in accord with the biological activity measured as total coliform bacterias per 100 ml (TC/100 ml) in the same sample. The values of TC/100 ml observed were (3–8) × 10^2; (0.4–6) × 10^4 and (0.5–4) × 10^4 for stations R, RA and SM respectively.

On average, the results presented in Table I are higher than those reported for sea waters of other coastal areas.[47-50] However, higher concentrations have been reported in polluted coastal marine waters including (ng kg^{-1}) Cd(5–452), Pb(18–2420), (Cu(130–3600); Cd(13–

Table I Heavy metal trace levels in Valparaíso sea coastal waters. Range values in the dissolved state ($\mu g\,l^{-1}$) for samples collected during 3 years (1981–1983)

Heavy metal	*Station*	*Natural pH*	*pH 2*	*pH 2 with UV irradiation*
Cd(II)	RA	*	0.2 –0.3	0.2 –0.4
	RAM	0.06–0.2	0.07–0.5	0.07–0.5
	R	0.06–0.3	0.12–0.4	0.1 –0.6
	SM	0.09–0.3	0.12–0.4	0.1 –0.4
Pb(II)	RA	0.5 –1.6	0.5 –3.2	0.7 –4.8
	RAM	0.2 –3.5	0.5 –3.9	0.4 –4.1
	R	0.3 –1.6	0.3 –1.8	0.3 –2.4
	SM	[illegible]	0.4 –4.5	
Cu(II)	RA	0.8 –3.0	2.4 –4.6	2.5 –7.1
	RAM	0.6 –2.3	0.6 –8.3	3.8 –9.6
	R	0.7 –2.4	1.0 –2.6	1.0 –3.8

* Not detected in the experimental condition.

390), Pb(41–7500), Cu(340–15 050) and Pb(1000–60 000), Cu(1000–41 000) in the Ligurian and North Tyrrhenian (Mediterranean sea), for Belgian and Dutch coast and for Kitakyushy District in Japan, respectively.[3,5,51] The large scatter and high values founded for Pb and Cu in surface waters should be due to suspended particles and sediments incorporated to the medium by antrophogenic sources and atmospheric contribution arising from the cities.

From the data obtained for distribution of heavy metals in sea water it is known that copper levels are higher than other metals. The copper enrichment in this Pacific ocean region should be explained by its proximity to a continental area close to copper mines where this metal is recovered and refined. It may have also a volcanic origin.

The highest concentration of metals is usually associated with local point sources of metal emission. The atmosphere, rivers and drainage contaminated by mining and smelting activities represent a very important medium in the global dispersion of environmental metal pollutants. This fact is reflected specially at the mouth of Aconcagua river (station RA and RAM) where highest values for copper where obtained.

Table II Heavy metal levels for sea water samples at pH 2, collected the same month during 3 years (June 1981–1983), (average in $\mu g\, l^{-1}$)

Station	*Heavy metal*	*Years* 1981	1982	1983
	Cd(II)	0.17	0.09	0.12
RA	Pb(II)	0.9	0.5	1.2
	Cu(HI) 3.8	1.7	6.5	
	Cd(II)	0.18	0.12	0.13
RAM	Pb(II)	1.1	0.3	0.9
	Cu(II)	4.1	2.2	8.7
	Cd(II)	0.10	0.12	0.13
R	Pb(II)	0.3	1.4	1.0
	Cu(II)	0.13	1.0	1.3
	Cd(II)	0.15	0.12	0.10
SM	Pb(II)	0.4	0.5	0.8
	Cu(II)	0.9	2.7	1.9

This was attributed to the proximity of this river to a copper mining and smelting area and a petrochemical factory. In general the copper concentrations showed considerable variation between the sampling. This behaviour was not observed for Cd(II) and Pb(II). (See Table II).

The values obtained for the surface metal concentration at different distances from the coast (station BV-5, BV-6 and the station at 22 miles) decrease in the direction of the open sea, reflecting the dilution effect (Table III).

Depth profiles of nutrients, dissolved oxygen and heavy metals

Depth profiles for nutrients like nitrates, phosphates and dissolved oxygen obtained for samples collected at 22 miles from the coast are showed in Fig. 3.

Profiles for nitrate and phosphate are similar. The levels are low in the surface zone due to nutrient consumption by phytoplankton, increase sharply to about 450 m, and from 500 m down to the bottom the nutrient concentrations increase marginally. Dissolved oxygen in

Table III Heavy metal levels for sea water samples collected the same day at different distances of coast ($\mu g\ l^{-1}$)

Station	*Natural pH*			*pH 2*		
	Cd	*Pb*	*Cu*	*Cd*	*Pb*	*Cu*
M	0.06	0.7	3.3	0.07	2.1	5.8
BV 5	0.04	0.5	1.5	0.06	1.2	3.3
BV 6	0.03	0.3	1.0	0.05	0.6	1.9
22 miles (32°45′ S, 72°00′ W)	*	*	*	0.04	0.3	1.2

*All sample was acidified.

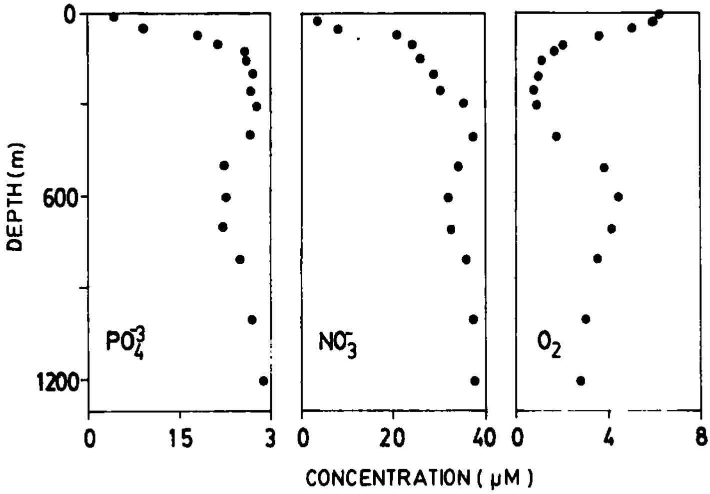

Figure 3 Depth profiles for nutrients nitrate, phosphate and dissolved oxygen for samples collected at 22 miles from coast (32°45′ S–72°00′ W).

contrast with nitrates and phosphates, decreases to very low value at about 200 m and increases below 400 m slowly towards the bottom. Similar profiles have been reported by other authors.[1,5,52–6]

Differences between nutrient concentration depending on depth, can be explained by the presence of different water masses with their own characteristics. In surface waters of subantartic origin nutrients concentration are low due to photosynthetic activity, but in deeper

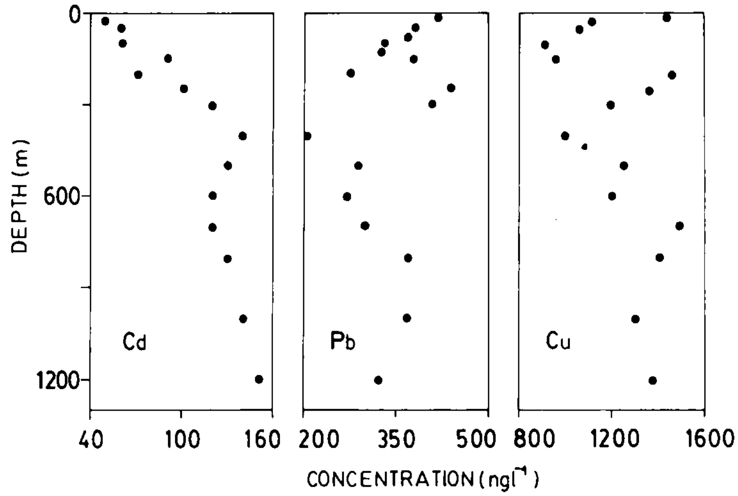

Figure 4 Depth profiles for heavy metals Cd(II), Pb(II) and Cu(II) for samples collected at 22 miles from coast (32°45′ S, 72°00′ W).

waters where phytoplanckton decrease and biochemical decomposition process increase, nutrients enrichment was observed.

Between 150–450 m exists an Ecuatorial water mass arising from Peru, with a greater salinity, a smaller dissolved oxygen concentration and higher nutrient concentration which could explain the before mentioned variations. Nurnberg *et al.*[57] in a study on the distribution of heavy metals in the Atlantic and Pacific oceans also found that waters into the Peru current are rich in nutrients.

Below 450 m to 700 m we found an Antartic water mass that presents a dissolved oxygen enrichment, decreasing salinity and nutrient concentration.

Vertical distribution of Cd(II), Pb(II) and Cu(II) concentration are showed in Fig. 4. Similar profiles for these metals were founded by other authors in other oceans.[1,5,17,52,54,56,58,59]

In surface waters the phytoplankton growth is stimulated by nutrient availability followed by uptake of Cd(II) that causes significantly lower dissolved cadmium concentration, showing then tendency towards increasing values with depth. Similar profile for Cd was found by Nurnberg *et al.*[57] in other Pacific region (01°09′ Sm 115°20′ W). In contrast to nutrients and cadmium, lead has a completely different behaviour and decrease with depth. The large scatter and high values founded for Pb and Cu in surface water to 150 m should be due to previously mentioned reasons.

Summarizing it was found that only nitrate, phosphate, dissolved oxygen and Cadmium present well defined profiles. Cadmium depth profile closely parallel the distribution of nitrate and phosphate. When Cd were plotted against NO_3^- and PO_4^{-3} concentrations a better correlation was established for Cd-NO_3^-. The resulting equation was: Cd $ngl^{-1} = -13.8 + 3.51$ (NO_3^-) (μM) with a correlation coefficient of 0.93 (n = 14). Similar results had been also reported by other authors in other ocean profiles.[1,5,52,53,56,57,58] Although this type of pattern is quite general, it shows in quantity significant dissimilarity in different parts of the ocean. Nurnberg *et al.*,[57] for example, had proposed that the significantly higher levels of Cu, Pb, and Cd founded in depth profiles in the North Atlantic compared with the Pacific Ocean correspond to global trends in atmospheric pollution transport and they found a significant increase of Cd contents from the surface to depth in the Pacific ocean.

Complexion capacity and conditional constant determination

A diagnostic approach to clarify the speciation capabilities of a natural water type is the complexation capacity determination. This is an empirical entity and was determined with the methodology proposed by Duinker and Kramer[11] and Nurnberg.[1,20] The complexation capacity corresponds to the equivalence point of the titration curve of a natural water with a metal standard solution, recording the metal peak height after each addition of metal solution. Copper(II) was used as titrant for its tendency to form rather stable complexes with many organic ligands[1,4,13,16,20,26,30,32,33,37,43] and for its abundance in the coastal areas of this Pacific Ocean region. The titration of samples collected at R and SM station were carried out, because they were the stations with lower and higher number of total coliform ml^{-1} respectively and their overall concentration of dissolved organic matter should must be different.

The results obtained for R station in samples at natural pH and pH 2 are shown in figure 5. The titration curve at natural pH present two

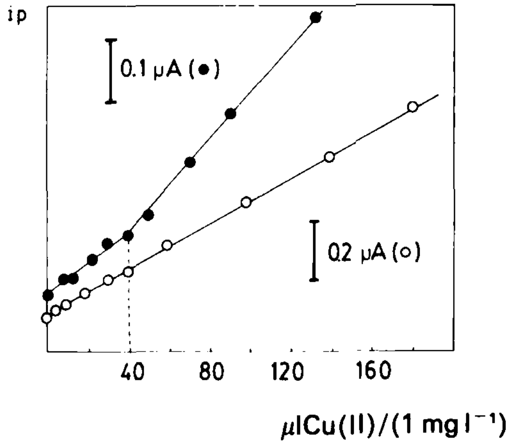

Figure 5 Determination of complexation capacity by voltammetric measurement. Titration graph for sea water sample at natural pH (●) and for the sample at pH 2 (○).

branches with different slopes (2.5 and 4.0 nA μl^{-1} respectively). In the first branche, a fraction of Cu^{+2} added is bound by organic ligands forming non-labile species. The voltammetric peak correspond to Cu^{+2} not bounded. When the whole amount of dissolved organic matter (DOM) able to bind Cu^{+2} has been consumed the second branch is obtained. The crossing point of two branches is the equivalence point, this behaviour, is not observable at pH 2 where the non-labile complexes are not stable. The complexation capacity of sea water for copper dissappears at low pH.

The complexation capacity determined for R and SM stations were 2 and 24 $\mu g\,l^{-1}$ Cu^{+2} respectively and they are included in the range values obtained for sea water samples.[4,7]

They are also in accordance with the results found for total coliform in the same samples. The high value of SM station is caused, undoubtedly, by a domestic waste discharge close to this station. This is not the case for R. station.

The other diagnostic approach, that has been obtained applying the voltammetric techniques in respect to non labile heavy metal complexes MeLm formed with organic ligands, is to determine the ligand concentration (L) required to achieve a certain degree of complexation under the effects exerted by the major chemical properties of the studied

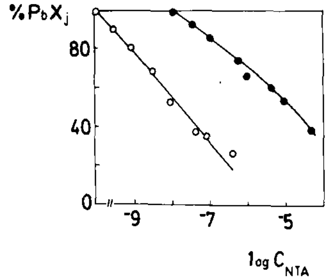

Figure 6 Relation between percentage of unchelated Pb^{+2} (present as labile complexes) and logarithm of chelating ligand concentration.
● synthetic solution 0.55 KCl suprapur, pH 5.
○ sea water sample at natural pH.

natural water type (salinity and pH). At 50% chelation the reciprocal of total ligand concentration correspond to K'.[25–38,47] In order to corroborate the validity of this model, pK' for Pb(II)-NTA complex was determinated in 0.55 M NaCl, pH 5 synthetic medium, Fig. 6. The value obtained 4.9 ± 0.3 have a good agreement with the data calculated applying the Ringbom methodology at the same ionic strength.[61] The results obtained for a sea water sample collected at R station (the same sample in which the complexation capacity was evaluated) are also shown in figure 6. The mean value for pK' was 7.5 and, this value indicates a low demand of NTA showing a poor competition degree of other trace metals dissolved in this natural sea water. The pK' reflects the operative specific influence of pH, salinity and other relevant metals Ca(II), Mg(II) on the formation of Pb(II)-NTA due to competition for the chelating ligand NTA.

These data obtained for sea water samples collected from a few sampling stations in the Pacific Ocean are a contribution to the knowledge on the distribution and speciation of trace heavy metal and their correlation with nutrients in sea waters.

Concentrations of trace metals in surface waters and depth profiles may be distinctly different in various parts of the oceans due to differences in the hydrographic and atmospheric parameters, the biological productivity and anthropogenic inputs. High anthropogenic inputs by rivers, run off and atmospheric deposition severely perturbate the natural mechanisms which tend to maintain a rather low steadystate level of dissolved trace metals. In coastal waters a continuous control of trace metals will be required in the future in order to follow the evolution of either increasing or decreasing toxic metal pollution.

ACKNOWLEDGEMENT

The authors are grateful to the Dirección General de Investigaciones, Universidad Católica de Valparaiso, Chile, for their financial support of this work. We thank also Professor Nelson Silva (Escuela de Ciencias del Mar de la Universidad Católica de Valparaiso) for his assistance and contributions in the course of this work and Dr. Professor Victoriano Campos *et al.* for the microbiological analysis (Laboratory of Microbiology, Universidad Católica de Valparaiso).

REFERENCES

1. H. W. Nürnberg, *Pure and Appl. Chem.* **54,** 853 (1982).
2. T. M. Florence, *Trends in Anal. Chem.* **2,** 162 (1983).
3. L. Mart, H. W. Nürnberg, P. Valenta and M. Stoeppler, *Thalassia Jugosl.* **14,** 171 (1978).
4. T. M. Florence and G. E. Batley, *Talanta* **24,** 151 (1977).
5. L. Mart, H. Rützel, P. Klahre, L. Sipos, U. Platzek, P. Valenta and H. W. Nürnberg, *Sci. Total Environ.* **26,** 1 (1982).
6. U. Förstner and G. T. W. Wittmann, Metal pollution in the aquatic environment (Springer-Verlag, Berlin, 1979).
7. H. W. Nürnberg, *Fresenius Z. Anal. Chem.* **316,** 557 (1983).
8. U. Förstner and W. Salomons, in G. G. Leppard (ed.), Trace element speciation in surface waters and its ecological implications (Plenum Press, New York, 1983), pp. 245–263.
9. H. W. Nürnberg, *Electrochim. Acta,* **22,** 935 (1977).
10. M. Bouzanne, *Analusis* **9,** 461 (1981).
11. J. C. Duinker and C. J. M. Krammer, *Mar. Chem.* **5,** 207 (1977).
12. M. I. Abdullah, B. Reusch Berg and R. Klimek, *Anal. Chim. Acta* **84,** 307 (1976).
13. S. R. Piotrowicz, M. Springer-Young, J. A. Puig and M. J. Spencer, *Anal. Chem.* **54,** 1367 (1982).
14. T. M. Florence and G. E. Batley, *J. Electroanal. Chem.* **75,** 791 (1977).
15. M. P. Landy, *Anal. Chim. Acta* **121,** 39 (1980).
16. H. W. Nürnberg and P. Valenta in Wong, Boyle, Bruland, Burton and Goldberg (eds.), Trace metals in sea water (Plenum Press, New York, 1980). pp. 671–697.

17. L. Mart, H. W. Nürnberg and D. Dyrssen, ibid., pp. 113–129.
18. T. Ugapo and W. F. Pickering, *Talanta* **32,** 131 (1985).
19. T. U. A. Analütia and W. F. Pickering, *Talanta* **34,** 231 (1987).
20. H. W. Nürnberg, *Thalassia Jugosl.* **16,** 95 (1980).
21. C. Guzmán O., *Alimentos* **12,** 42 (1987).
22. J. O. Leckie and R. O. James, in: A. J. Rubin (ed.), Aqueous environmental chemistry of metals (Ann arbor Science Pub. Inc., Michigan, 1976), Chap. 6, p. 21.
23. M. Fayyad, *Anal. Chem.* **59,** 209 (1987).
24. A Voulgaropoulos, P. Valenta and H. W. Nürnberg, *Fresenius Z. Anal. Chem.* **317,** 367 (1984).
25. B. Raspor, H. W. Nürnberg and P. Valenta, *Limnol. Oceanogr.* **26,** 54 (1981).
26. J. R. Tuschall Jr. and P. L. Brezonik, *Anal. Chem.* **53,** 1986 (1981).
27. B. Raspor, P. Valenta, H. W. Nürnberg and M. Branica, *Sci. Total Environ.* **9,** 87 (1977).
28. H. W. Nürnberg and B. Raspor, *Environ. Tech. Lett.* **2,** 457 (1981).
29. G. E. Batley, in: G. G. Leppard (ed.), Trace element speciation in surface water and its ecological implications, (Plenum Press, New York, 1983), pp. 17–36.
30. H. W. Nürnberg, *Fresenius Z. Anal. Chem.* **316,** 557 (1983).
31. B. Raspor, H. W. Nürnberg, P. Valenta and M. Branica in: M. Branica and Z. Konrad (ed.), Lead in the Marine environment, (Pergamon Press, Oxford, 1980), pp. 181–195.
32. M. S. Shuman, *Anal. Chem.* **54,** 98 (1982).
33. J. R. Tuschall and P. L. Brazonik, *Anal. Chem.* **54,** 2116 (1982).
34. H. W. Nürnberg, P. Valenta, L. Mart, B. Raspor and L. Sipos, *Z. Anal. Chem.* **282,** 357 (1976).
35. F. L. Greter, J. Buffle and W. Haerdi, *J. Electroanal. Chem.* **101,** 211 (1979).
36. S. D. Brown and B. R. Kowalsky, *Anal. Chem.* **51,** 2133 (1979).
37. B. Lazar and A. Katz, *Mar. Chem.* **10,** 221 (1981).
38. W. F. Jardim, The use of electroanalytical techniques to measure copper complexation by naturally occurring ligands, Simp, Bras. Electroquim. Electroanal., ANAIS (1984), pp. 167–172.
39. A. Zirino and S. Yamamoto, *Limnol. Oceanogr.* **17,** 661 (1972).
40. J. Buffle, Trends in: *Anal. Chem.* **1,** 90 (1981).
41. T. M. Florence, *Anal. Chim. Acta* **141,** 73 (1982).
42. G. E. Batley and J. Farrar, *Anal. Chim. Acta* **99,** 283 (1978).
43. T. M. Florence, *Talanta* **29,** 345 (1982).
44. G. Charlot, Chimie Analytique Quantitative, Vol. II. (Maisson et Cie, Paris, 1974), p. 485.
45. Ibid., p. 437.
46. J. H. Carpenter, *Limnol. Oceanog.* **10,** 141 (1965)
47. B. Raspor, in: J. O. Nriagu, (ed.), Cadmium in the environment, Part 1, Ecological cycling (John Wiley and Sons, New York, 1980), Ch. 6., p. 147.
48. V. Förnstner and G. T. W. Wittmann, Metal pollution in the aquatic environment (Springer-Verlag, Berlin, 1979), p. 71.
49. E. A. Boyle, in: J. O. Nriagu (ed.), Copper in the environment, Part 1: Ecological cycling (John Wiley and Sons, New York, 1979), pp. 78–81.

50. M. Bernhard, in: M. Branica and Z. Konrad (ed.), Lead in the marine environment (Pergamon Press, New York, 1980), pp. 345–352.
51. H. Sakino, A. Haskimoto, Y. Uchimura, S. Tatrishi and T. Akiyama, *Water Research* **14**, 1233 (1980).
52. E. A. Boyle, F. Sclater and J. M. Edmon, *Nature* **263**, 107 (1976).
53. E. Boyle and J. M. Edmond, *Nature* **253**, 107 (1975).
54. J. M. Martin, G. A. Knauer and A. R. Flegal, in: J. O. Nriagu (ed.), Cadmium in the environment, Part 1, Ecological cicling (John Wiley and Sons, New York, 1980), Ch. 5, pp. 141–145.
55. M. O. Andreae, *Limnol. Oceanogr.* **24**, 440 (1979).
56. K. W. Bruland, G. A. Knauer and J. H. Martin, *Limnol. Oceanogr.* **23**, 618 (1978).
57. H. W. Nürnberg, L. Mart, H. Rützel and L. Sipos, *Chem. Geology* **40**, 97 (1983).
58. L. G. Danielsson, *Mar. Chem.* **8**, 199 (1980).
59. K. W. Bruland and R. P. Franks, *Anal. Chim. Acta* **105**, 233 (1979).
60. R. M. Moore and J. D. Burton, *Nature* **264**, 214 (1976).
61. A. Ringbom, Les complexes en chimie analytique (Dunod, Paris, 1967).