
Use of speciation modelling of heavy metals in Los Patos lagoon, Argentina, to improve waterbody management

**Erica Y. Sanchez*, Lucila Elordi
and Soledad Represa**

Centro de Investigaciones del Medio Ambiente (CIMA),
Facultad de Ciencias Exactas (FCE),
Universidad Nacional de La Plata (UNLP),
47 y 115, La Plata, Prov. Bs. As., Argentina
Email: yaninasanch@quimica.unlp.edu.ar
Email: lucilaelordi@hotmail.com
Email: sol.represa@gmail.com

*Corresponding author

Leonardo Cano

Centro de Investigaciones del Medio Ambiente (CIMA),
Facultad de Ciencias Exactas (FCE),
Universidad Nacional de La Plata (UNLP),
47 y 115, La Plata, Prov. Bs. As., Argentina

and

Programa Ambiental de Extensión Universitaria,
FCE-UNLP 50 y 115, La Plata, Prov. Bs. As., Argentina
Email: lcano@quimica.unlp.edu.ar

Esteban Colman Lerner

Centro de Investigación y Desarrollo en Procesos Catalíticos
(CINDECA)-CONICET-UNLP,
47 N° 257, La Plata, Prov. Bs. As., Argentina
Email: jecolman@quimica.unlp.edu.ar

Santiago Elisio and Dario Andrinolo

Centro de Investigaciones del Medio Ambiente (CIMA),
Facultad de Ciencias Exactas (FCE),
Universidad Nacional de La Plata (UNLP),
47 y 115, La Plata, Prov. Bs. As., Argentina

and

Programa Ambiental de Extensión Universitaria,
FCE-UNLP 50 y 115, La Plata, Prov. Bs. As., Argentina
Email: santielisio@gmail.com
Email: dandrinolo@yahoo.com

Andres Porta

Centro de Investigaciones del Medio Ambiente (CIMA),
Facultad de Ciencias Exactas (FCE),
Universidad Nacional de La Plata (UNLP),
47 y 115, La Plata, Prov. Bs. As., Argentina
Email: aaporta@yahoo.com.ar

Abstract: Levels established in water quality guidelines for the protection of aquatic life are based on the total concentrations of heavy metals regardless of speciation. However, there are numerous studies that show the importance of determining both the physicochemical characterisation of water body and the total concentration of heavy metals in them, including its chemical speciation, given its specific correlation with the bioavailability. In this regard, the objective of this study is to quantify concentrations of heavy metals in Los Patos lagoon, Argentina, and to show the utility of estimating with Visual MINTEQ software the fractions in which these metals are forming aqueous inorganic species or complexed with organic matter. The results demonstrate the relevance of using speciation calculations of metal cations, particularly when their concentrations are in the order of guide levels.

Keywords: Visual MINTEQ; speciation; bioavailability; trace metals.

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Biographical notes: Erica Y. Sanchez is working at the Institute of Environmental Studies as a Scientist, in the Universidad Nacional de la Plata. She does research about dispersion of pollutants in the atmosphere. Specifically, she is developing numeric models. Besides, she is a Teacher in charge of the practical lessons in the subject "Models of Dispersion and Environmental Distribution of Pollutants".

Lucila Elordi is a Teacher in charge of the practical lessons of Environmental Program of University Extension at the National University of La Plata. She received her Doctorate in Biology from National University of La Plata. Her current research interests include the physico-chemical and biological monitoring of water bodies.

Soledad Represa received her degree in Chemistry and Environmental Technology. Currently, she is a PhD student in Chemistry at UNLP. Her research areas include the application of remote sensing in the study of air quality and the use of GIS for risk maps.

Leonardo Cano graduated in Chemistry from the Universidad Nacional de La Plata (2006), PhD in Exact Sciences from the same University (2011). He is a Researcher of CONICET since 2013 with projects in the area of environment, pollution of water and disposal of pollutants. He is also a Teacher in charge of the practical lessons in the subject: "Transport Phenomena".

Esteban Colman Lerner is working at the Center for Research and Development of Applied Science (CINDECA) as a Scientist at the National Council of Scientific and Technical Research (CONICET). His research is

developed on the levels of Volatile Organic Compounds (VOCs) and Material Particulates (MP) in the atmosphere and development of catalytic methods to mitigate its impact. In addition, he is a Teacher in charge of the practical classes of subjects “Analytical Chemistry Environmental” and “Analytical Chemistry Applied” at the National University of La Plata.

Santiago Elisio received his degree in Chemistry Engineering from the National University of La Plata. Currently, she is a PhD student in Chemistry at UNLP.

Dario Andrinolo is a Director of Environmental Program of University Extension at the National University of La Plata. He is an Independent Researcher of the National Council of Scientific and Technical Research (CONICET). His field of research includes environmental toxicology.

Andres Porta is a Vice Director of the Environmental Center (CIMA) at the University of La Plata. He is an Independent Researcher of Scientific Research Commission of the Province of Buenos Aires. He is also a Professor of Analytical Chemistry and Models of Dispersion and Environmental Distribution of Pollutants”. His field of research includes environmental toxicology and chemistry, particularly referred to air pollution.

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1 Introduction

Constant growth of cities and occupation of natural areas with housing and industrial purposes, leading to the detriment of these areas and environmental quality, constantly generates socio-environmental conflicts. These are multi-causal in nature, and highlight the need for specific studies on pollution of water resources.

In addition, technology development and industrialisation are factors contributing to emission into the atmosphere, continuously, of a large number of toxic substances. These can be defined as compounds that exceed natural concentrations in a system and cause negative impacts on the environment (Albert, 1999). Some examples are pesticides, oils and fats, hydrocarbons and heavy metals, among others (Hart and Fuller, 1974).

Many of the pollutants that enter into a body of surface water by natural or anthropogenic means are retained in sediments deposited at the bottom of the channel, thus impacting on aquatic systems (Bohn et al., 2001; Esteves et al., 1996). These deposits, by interacting with the streams, retain contaminants thus altering the overall dynamics of the water mass (Mariani and Pompeo, 2008). Thus, variations in pH, salinity and the redox properties of the water currents can cause mobilisation and resuspension of chemical species accumulated in the sediments, even magnifying any toxic effect, as is the case of heavy metals (Ruiz et al., 1994).

Nowadays, it is entirely accepted that the toxicity and mobility of heavy metals depend primarily on their chemical form and how they are linked or attached to the solid matrix, or to inorganic and organic ligands present in the aqueous matrix. Examples of

interest are Hg, As, Cr, Pb, Cd, Ni and Zn, since for most organisms exposure above a threshold concentration can be harmful (Martinez Tabche et al., 2000). Ions of these items typically enter the cell through the same transport systems that are used by other physiologically important metal cations. Uptake and toxicity of heavy metals to aquatic organisms are influenced not only by their concentration, but also by their relevance to exposure time and biotic and abiotic environmental factors (Dawson and Ballatori, 1995; Markert, 1998; Wilken, 1998).

The behaviour of a metal depends on the particular species in which it is present and its reactivity does not necessarily coincide with the total concentration of metals in the environment. Hence, the behaviour of an element in the environment (bioavailability, toxicity, distribution, etc.) cannot be predicted only based on their total concentration (Bernhard et al., 1986).

To describe the behaviour of trace elements in the environmental matrix, the term 'speciation' is incorporated. Chemical speciation is defined as the distribution of a chemical element between the different forms in which it can exist (species) in a particular environment. It includes both free elements (neutral or ionised form) and the various complexes that can be formed with different ligands (Lyman, 1995). The chemical speciation in surface waters reflects the chemical complexity of that environment.

Speciation models for trace elements consider their complexing with inorganic and organic low molecular weight ligands, association with dissolved organic matter (DOM), adsorption on the surface of the particulate material, redox reactions, etc. (Castañé et al., 2003). Currently, the code Visual MINTEQ is one of the programs widely used in geochemistry modelling, and the use of code Visual MINTEQ allows modelling the balance and speciation of inorganic and organic solutes, and also determines the states of saturation with respect to different minerals phases in the system and, consequently, the direction of the reactions that may occur to reach equilibrium.

Research involving chemical speciation models have been reported in scientific journals of international publication; some of them describe patterns of behaviours related to transport, mobilisation and solubilisation of different elements into simple and complex aqueous systems, including modelling of chemical species of arsenic, mercury, cadmium, copper, lead and others in natural environments and in other environments modified by human activities (Arrieta et al., 2000; Mason and Jenkins, 1995; Santore et al., 2001). As Han et al. (2014), Meck et al. (2011) and Sjöstedt et al. (2009) show in their works, the MINTEQ software is useful and helpful for studying speciation in lakes and rivers, and to analyse the bioavailability of metals for risk assessment in aquatic species (Kawanishi, 1995; Rosenberg et al., 1998; US EPA, 2001).

Particularly, Los Patos lagoon, located in the district of Ensenada (middle basin of the Rio de La Plata) in the Province of Buenos Aires, Argentina, is a lagoon of interest to directing specific studies of environmental pollutants and its impact, since it is located in a region with constant residential and industrial growth, and little is known about these aspects (InfoGEI, 2015; Newspaper 'El Día', 2015). As well it shows the landscape, the lagoon has a rich variety of flora and fauna in an area in which coexist industries, processing plant waste, recreational areas and population centres (suburbs of Punta Lara, Villa del Plata and Piria). Its artificial origin (quarry land and crude) has not limited its insertion into the landscape of the region as an aquatic ecosystem that is attractive for decades (Gimenez et al., 2010; IDEBA, 2015).

Los Patos lagoon has a rectangular shape and an area of 0.2 km². In it, you can spot species such as black-necked swans, cutirí ducks, coots, red gusset, bataraces woodpeckers, sparrows, Tachuris seven colours, herons, chimangos, starlings and screamers. Its flora includes logging, ceiba, willows and vines (Birds in Focus, 2015).

In the last period, the mass media have made known to society different works in the private sector that would affect the dynamics of the water body (InfoGEI, 2015; Newspaper 'El Día', 2015).

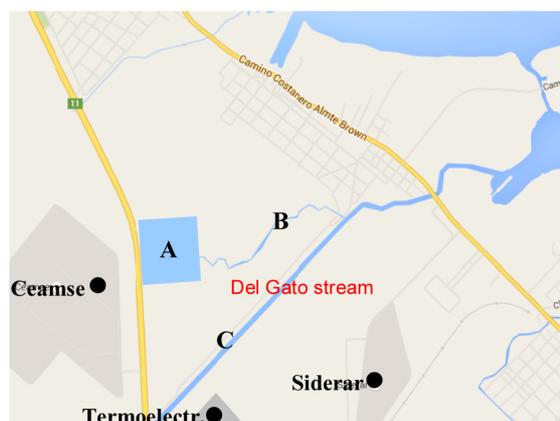
The aim of this study is to quantify the levels of heavy metals in the lagoon, and modelling (with Visual MINTEQ software) the fractions in which these metals are forming aqueous inorganic species or complexed with organic matter, evidencing the relevance to know the labile fraction of metals vs. total concentrations for comparing it with guide levels.

2 Methodology

2.1 Sampling site

As shown in Figure 1, Del Gato stream flows through the ground in SW-NE, and lagoon communicates with the stream by a small channel of just over 1 km called the Zanjón, and the whole system ends later in the Santiago River to finish in the river of La Plata. To the left of the lagoon is Diagonal 74 Street, the main route of communication between Punta Lara and the city of La Plata, which is a physical division with the sanitary landfill of *Coordinación Ecológica Área Metropolitana Sociedad del Estado* (CEAMSE).

Figure 1 Map of the study area: *Los Patos* Lagoon (A), *El Zanjón* stream (B) and *Del Gato* stream (C) (see online version for colours)



2.2 Sample collection and physicochemical characterisation

Under sampling standards presented in Eaton et al. (1998), a single sample of lagoon in each of the months of December 2014 and March 2015 was taken.

The following in situ parameters were measured using a multiparameter probe – SPER CIENTIFICO for environmental quality: temperature, pH, dissolved oxygen (DO) and conductivity.

In the laboratory, we analysed different physicochemical parameters in water samples, following the standard methods presented in Eaton et al. (1998). From here on, in parenthesis it shows the number of methods used.

For chlorides, we used the titration method with silver nitrate, using chromate as an end point indicator (S.M. 4500-Cl-B); alkalinity was measured titrating with HCl and phenolphthalein and bromocresol green as indicators (S.M. 2320 B).

For the determination of the sulphate content, the turbidimetric method was used, forming BaSO₄ from the reaction of the sample with BaCl₂ and reading the light absorbance of the suspension in a WGZ-20 Turbidimeter of Shanghai Xinrui Instruments and Meters co., Ltd. (S.M. 4500-SO4- E).

Phosphates were measured from the reaction with (NH₄)₆Mo₇O₂₄ and SnCl₂ to form deep-coloured molybdenum blue, which is measured at 690 nm in a UV-Vis BIO TRAZA spectrophotometer model 752 (S.M. 4500-P D).

The chemical oxygen demand (COD) was determined by oxidation of the sample with K₂Cr₂O₇ in closed reflux, then measuring unreacted dichromate in a UV-Vis BIO TRAZA spectrophotometer at 600 nm (S.M. 5220 D).

The content of metals (Fe, Ni, Cu, Zn, Pb, Hg, Ca, Mg, K and Na) was obtained by ICP-MS with 350 NexION equipment of Perkin Elmer, quantifying it by external calibration curve. Previously, the aqueous samples were digested by microwave (MARS 6).

2.3 Speciation modelling

Visual MINTEQ 3.1 software was used to calculate the speciation of the metal cations in this work, by estimating the composition of aqueous dilute solutions in equilibrium with the solid phase. Through it, the mass distribution of the dissolved species is established and absorbed in multiple solid phases, for various conditions. This software has an extensive database of thermodynamic data, suitable for solving a wide variety of problems without obtaining additional equilibrium constants (Allison et al., 1991; Bethke, 2008; Felmy et al., 1984).

As input, it requires a chemical analysis of the sample of the lagoon (conductivity, pH, chloride, alkalinity, sulphate, phosphate and dissolved organic carbon (DOC)), concentrations of compounds of interest (iron, nickel, copper, zinc, lead, mercury, calcium, potassium and sodium) and other relevant variables for the system as the water temperature. Modelling results are exported as a file extension *.xls for further processing.

3 Results and discussion

Values of physicochemical parameters and total concentrations of metals obtained in the monitoring of December (DM) and March (MM) are exposed in Table 1. These preliminary results show that the total concentrations of some metals under study, such as Pb, Hg and Cu, exceed levels established in guidelines (GL) for natural water quality (national and provincial) in both sampling campaigns, and also that heavy metals concentrations in DM were higher than those for MM by at least one order of magnitude.

Table 1 Values of physicochemical parameters and total concentrations of metals

<i>Parameter</i>	<i>Units</i>	<i>DM</i>	<i>MM</i>	<i>Method</i>	<i>GL (protection of aquatic life)</i>
Temperature	°C	18.4	25.5	SM 2550	(***)
Conduct.	mS	0.275	0.643	SM 2510	(***)
pH	U pH	7.8	6.8	S.M. 4500-H+B	6.5-9.0 (**)
DO	mgO ₂ /L	8.3	8.2	S.M. 2515	≥5 (*)
DOC	mg/L	2.5	19.4	Allison (1965)	(***)
Phosphate	µg/L	342.0	237.0	S.M. 4500-P	(***)
Chlorides	mg/L	42.3	98.2	SM 4500-Cl ⁻ B	(***)
Sulphates	mg/L	2.56	1.0	SM 4500-SO ₄ ⁼ -E	(***)
Alkalinity	mg HCO ₃ ⁻ /L	77.0	149.4	SM 2320 B	(***)
Fe	µg/L	831.0	30.4	SM 3125	1370 (*)
Ni	µg/L	14.7	0.2	SM 3125	17.3 (*); 6.34 (**)
Cu	µg/L	22.0	2.1	SM 3125	0.95 (*); 0.45 (**)
Zn	µg/L	52.6	1.4	SM 3125	9.3 (***)
Pb	µg/L	9.4	2.1	SM 3125	0.6 (*); 0.52 (**)
Hg	µg/L	11.7	1.0	SM 3125	0.029 (*); 0.77(**)
Na	mg/L	55	79.8	SM 3125	(***)
K	mg/L	5.3	7.9	SM 3125	(***)
Ca	mg/L	7.5	15.0	SM 3125	(***)

*Secretary of Water Resources of the Nation, Argentina.

**Resolution 42/06 of Water Authority of the Province of Buenos Aires.

***No guide values in (*) or (**).

The results modelled with Visual MINTEQ software (Table 2) show that only Cu, Hg and Pb (DM), and Hg, Pb, Ni, Cu and Fe (MM) are present both as aqueous inorganic species and complexed with DOM, in greater proportion; however, these last fractions do not prevent that DM overcoming GL.

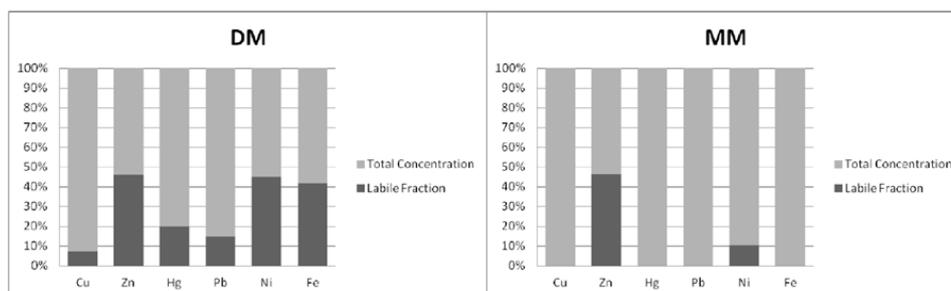
The complexes between metallic cations and DOM, frequently referred as DOC and in MINTEQ as fulvic acid (FA), are characterised by high stability resulting in a low bioavailability of these metals for the aquatic biota. There are also another complex with high stability with the participation of inorganic ligands, as carbonates and hydroxides (Reeder et al., 2006; Worms et al., 2006). Bioavailability is a complex process that involved basically the ability of the biota to displace the complexed metal, assuming a competition process between DOC, inorganic ligands and biotic ligands for the metals. Also, usually is considered the mitigating effects of competition with other cations (e.g., Ca²⁺, Na⁺) and protons for binding to the biotic ligand (Rüdel et al., 2015; Santore et al., 2001). MINTEQ analyses this situation as a multiple equilibrium situation, and the quantification occurs using the equilibrium constant. Thus, it is possible to provide the remaining fraction under conditions of rapid availability or accessibility (labile fraction). In this aspect, labile fractions 8, 84, 25, 17, 82 and 71% for the first sampling (DM), and 0, 87, 0, 0, 12 and 0% for the second sampling (MM) were observed for Cu, Zn, Hg, Pb, Ni and Fe, respectively (Figure 2).

Table 2 Percentage distribution of species

	<i>DM</i>		<i>MM</i>	
	<i>Total concentración (%)</i>	<i>Species name</i>	<i>Total concentración (%)</i>	<i>Species name</i>
Fe^{+3}	71.484	$\text{Fe}(\text{OH})_2^+$		
	1.674	$\text{Fe}(\text{OH})_3$ (aq)	100	FA-Fe(III)(6)(aq)
	1.096	$\text{Fe}(\text{OH})_4^-$		
	25.736	FA-Fe(III)(6)(aq)		
Ni^{+2}	77.733	Ni^{+2}	9.445	Ni^{+2}
	0.313	NiOH^+	0.174	NiCO_3 (aq)
	0.025	NiCl^+	2.113	NiHCO_3^+
	0.098	NiHPO_4 (aq)	85.965	FA-Ni(6)(aq)
	6.453	NiCO_3 (aq)	2.26	(6)Ni+2D(aq)
	7.780	NiHCO_3^+	0.016	(6)NiHCO ₃ +D(aq)
	3.668	FA-Ni(6)(aq)	0.01	NiSO_4 (aq)
	3.677	(6)Ni+2D(aq)		
	0.216	NiSO_4 (aq)		
	0.024	$\text{Ni}(\text{OH})_2$ (aq)		
Cu^{+2}	3.708	Cu^{+2}		
	4.343	CuOH^+		
	0.279	$\text{Cu}(\text{OH})_2$ (aq)		
	0.069	CuHPO_4 (aq)		
	48.78	CuCO_3 (aq)	100	FA-Cu(6)(aq)
	0.190	CuHCO_3^+		
	0.518	$\text{Cu}(\text{CO}_3)_2^{-2}$		
	0.175	(6)Cu+2D(aq)		
	0.011	CuSO_4 (aq)		
	41.913	FA-Cu(6)(aq)		
Zn^{+2}	78.073	Zn^{+2}	69.49	Zn^{+2}
	2.409	ZnOH^+	6.965	FA-Zn(6)(aq)
	2.985	$\text{Zn}(\text{OH})_2$ (aq)	0.365	ZnOH^+
	0.192	ZnCl^+	1.986	ZnCO_3 (aq)
	0.225	ZnHPO_4 (aq)	0.410	ZnCl^+
	10.038	ZnCO_3 (aq)	0.082	ZnSO_4 (aq)
	2.004	ZnHCO_3^+	0.063	ZnHPO_4 (aq)
	0.130	FA-Zn(6)(aq)	3.986	ZnHCO_3^+
	0.237	ZnSO_4 (aq)	0.026	$\text{Zn}(\text{OH})_2$ (aq)
	3.693	(6)Zn+2D(aq)	16.626	(6)Zn+2D(aq)
	0.014	$\text{Zn}(\text{CO}_3)_2^{-2}$		

Table 2 Percentage distribution of species (continued)

	DM		MM	
	Total concentración (%)	Species name	Total concentración (%)	Species name
Pb ⁺²	8.252	Pb ⁺²	0.021	Pb ⁺²
	62.473	PbCO ₃ (aq)	0.035	PbCO ₃ (aq)
	13.830	FA-Pb(6)(aq)	0.030	PbHCO ₃ ⁺
	8.567	PbOH ⁺	99.906	FA-Pb(6)(aq)
	0.199	Pb(OH) ₂ (aq)		
	0.248	PbCl ⁺		
	0.059	PbSO ₄ (aq)		
	0.015	PbHPO ₄ (aq)		
	0.634	Pb(CO ₃) ₂ ⁻²		
	5.332	PbHCO ₃ ⁺		
Hg ⁺²	0.390	(6)Pb+2D(aq)		
	32.642	Hg(OH) ₂		
	3.596	HgCl ₂		
	0.043	HCl ₃ ⁻¹		
	23.582	HgClOH(aq)	100	FA-Hg(6)(aq)
	0.047	HgCO ₃ (aq)		
	0.378	HgOHCO ₃ ⁻		
	39.705	FA-Hg(6)(aq)		

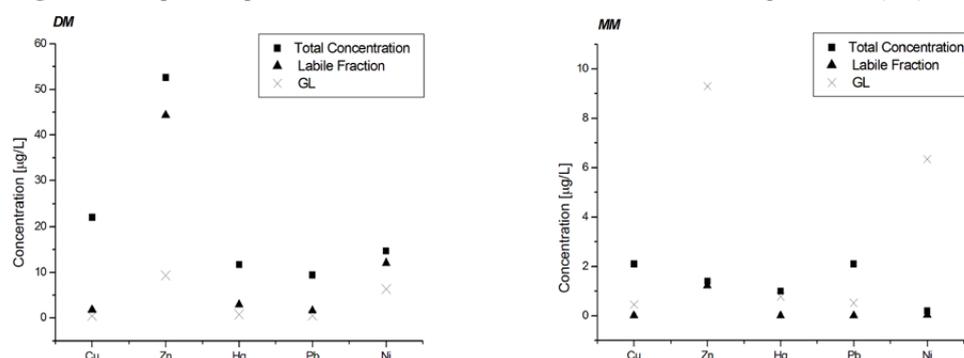
Figure 2 Percentage ratio between the total and labile concentration for December monitoring (DM) and March monitoring (MM)

The sample DM besides presenting high values of total metal concentrations shows low proportions of organic matter, which together manifests higher values of labile fractions of the metal cations compared with the values observed in sample MM. The decreased levels of metals in the sample March with respect to DM shown in Table 1 (1–2 orders of magnitude) could be explained by the increase in blooms of *Pistia stratiotes* between January and March 2015, with proven ability for uptake of metals (Cd and Hg), and contribute to the removal of ammonium nitrogen and phosphorus

(Putra et al., 2015; Tripathi et al., 2010). Moreover, the variability of the metal speciation percentage in both scenarios (Table 2) could be attributed to the marked difference in the values of DOC.

The results show that if the total concentrations of metals are in the order of the guide levels, it is essential to study the speciation and bioavailability to quantify the risk that they represent and thus develop an appropriate management (Figure 3). However, when the total metal concentration exceeds one or more orders of magnitude to the reference values, the role of speciation is of lower relevance.

Figure 3 Graphical representation of the total and labile concentration, and guide level (GL)



As shown in Table 2, it is observed that not all metals have the same affinity for inorganic ligands, without taking into account the affinity for organic matter, since Ni^{+2} , Cu^{+2} , Zn^{+2} and Pb^{+2} are found as free metal or bound to the carbonate species ($\text{HCO}_3^- / \text{CO}_3^{2-}$), whereas Fe^{+3} and Hg^{+2} have more affinity to OH^- (and Pb^{+2} to a lesser extent). Ni^{+2} , Cu^{+2} , Pb^{+2} , Zn^{+2} and Hg^{+2} form complexes with Cl^- , HPO_4^- and SO_4^- ligands, with little relevance.

Finally, as all surface water body has a natural dynamic in which the parameters are modified cyclically, so it is necessary to know the maximum and minimum values at different stages of the cycle for complete management. The results of this study demonstrate the importance of knowing speciation for the implementation of specific regulatory mechanisms, such as the law allowed effluent and wastewater discharged. Indeed, European and US legislation incorporates these criteria with different modalities, driven by the use of software features as MINTEQA2.

4 Conclusions

These results demonstrate the relevance of using speciation analysis of metal cations in particular when their concentrations are in the order of levels or reference guide. In this study, this situation occurs with bioavailability reductions of 100% for Pb, Hg and Cu. However, when the concentrations are higher than the reference values, the complexation effect decreases and loses its decisive significance.

Preliminary results manifest a complex dynamic of the lagoon, showing a high variability in individual monitored parameters. In this aspect, it is necessary a more detailed assessment of the lagoon, including analysis of metals in *P. stratiotes*, together

with the characterisation of their sediments that can be used as a solid phase interaction in the model, and thus achieve a more representative evaluation stage.

A final comment raises the need to incorporate this type of analysis for improving the management and assessing the potential risk that can be found in the water bodies, without forgetting that the models are only a representation of a real system and the goodness of their results depends mainly on the quality of the input data. In this aspect, it is important to ensure the application of standard analytical methods and to include a validation stage of modelling results through laboratory studies of speciation dynamics.

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