



## Seasonal Variation of Dissolved Lead Speciation in Tagus Estuary, Portugal

M. Praveen Kumar<sup>\*(\*\*)</sup>†

\*Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

\*\*N.B.K.R. Institute Of Science and Technology, Vidyanagar, S.P.S.R Nellore, Andhra Pradesh, India

†Corresponding author: M. Praveen Kumar; praveenm@nbkrist.org

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### ABSTRACT

The behavior of lead species from Tagus estuarine water collected during winter (January), spring (April), and summer (June) seasons were evaluated. Water samples were titrated with  $Pb^{2+}$  followed by differential pulse anodic stripping voltammetry (DPASV). Experimental voltammetric values were interpreted assuming a macromolecular heterogeneous ligand described in a simple way by two types of binding sites,  $C_{L1}$  and  $C_{L2}$ , where  $C_{L1}$  is related to stronger binding groups with lower concentration compared to  $C_{L2}$ . Water quality parameters like dissolved organic matter (DOC), pH, salinity, temperature, and total lead concentration were measured during the period under study. The results pointed to a higher concentration of  $C_{L1}$  and  $C_{L2}$  sites in April probably due to the phytoplankton bloom. The decrease of  $K_{L1}$  with the increase of salinity from winter to summer may be caused by the increase of major cations (as  $Ca^{2+}$ ) in solution. The trend of  $K_{L2}$  followed the pH shift in all seasons since an increase of pH favors  $Pb^{2+}$  complexation with  $C_{L2}$  sites. Finally, the decrease of DOC in summer could be responsible for the decrease in the concentration of the different sites in solution from April to June, with a similar decrease of  $35\pm 3\%$  for all of them.

### INTRODUCTION

Estuaries are natural water bodies with connections from the river to open sea waters (Pritchard 1967). Mixing of both marine and river waters provides a high level of nutrients, making estuaries the most productive natural habitat (McLusky & Elliott 2004). Estuaries receive a large number of pollutants from effluents if located nearby urban and industrial areas (Reboreda & Caçador 2007, Begona et al. 2020), and play a crucial role in metal transport mechanisms from the river to estuary and estuary to the ocean (Duarte & Caçador 2012, Anderson et al. 2016). The mechanism of metal distribution in salt marsh mainly depends on the physical and chemical conditions of the river and sea waters (Oursel et al. 2013).

Generally, estuaries have rich dissolved organic compounds with different ligand sites which can significantly influence the metal biogeochemical system (Martin et al. 2020). Metal complexation with organic ligands will change significantly metal bioavailability to organisms (Paiva et al. 2015). It is also important to determine the complexing strength because even weak binding sites also may affect significantly metal bioavailability if they are present in large concentrations (Buck & Bruland 2005). Speciation of trace metal in estuaries largely depends on local geochemical factors such as oxides and carbonates, as well as on biogenic particles and organic soluble compounds (Almeida et al. 2004, Anthony et al. 2015).

The studied area of this work, the Tagus estuary, is an important ecosystem in Portugal and one of the largest estuaries on the Atlantic coast of Europe, covering an area of about  $320 \text{ km}^2$ . Estuaries are natural sinks for heavy metal pollution. Numerous worldwide studies that focused on the behavior of lead in estuarine waters have shown that it varies from one estuary to another and depends on the time of the year as well as on river-estuarine-sea water mixing zones (Elbaz-Poulichet et al. 1996, Baeyens et al. 1998, Chiffolleau et al. 1994, Matthieu et al. 2007, Martino et al. 2007 & Oursel et al. 2013). A significant number of works have been focused on the distribution of lead and other heavy metals in the Tagus estuary and on the influence of different factors in that process, such as tidal and depth profile (Carlos 1990), flood episodes (Duarte & Caçador 2012), plants (Caçador et al. 1996, Reboreda & Caçador 2007), and sedimentation (Caçador et al. 2000). In the aquatic system, metal toxicity and mobility mainly depend on species distribution rather than on total metal concentration (Mota & Goncalves 1996). Knowledge of trace metal speciation in estuaries is important to understand the biogeochemical cycle. Few papers have reported lead speciation in Tagus estuary (Lindim et al. 2000, Mota et al. 2005), but no data have been published on the influence of the time of the year on lead speciation to the best of our knowledge. The present work is focused on the seasonal variation of lead speciation in the soluble fraction and its correlation with the trend observed for several

parameters such as DOC, pH, and salinity from the winter to summer months.

## MATERIALS AND METHODS

### Sampling Site and Sample Collection

Tagus river, the longest river of the Iberian Peninsula covering nearly 1038 km long, is the main source of fresh water supply to the Tagus estuary. This is one of the biggest estuaries on the Atlantic coast of Europe where it ends in the Atlantic Ocean near Lisbon. Tagus estuary covers nearly 320 km<sup>2</sup> comprising a deep, narrow, straight channel, and a wide and shallow inner bay. A large portion of effluents is received from urban and industrial activities. The sedimentation is mainly composed of fine/medium sand, silt, and clay with organic matter. The sampling area receives the flood tide twice a day, with tidal amplitude between 1.5 and 3.2 m (Silva et al. 2013).

Water samples were collected from Tagus estuary, in the saltmarsh of Corroios (38° 39.242' N, 9° 07.700' W) at the end of the low tide during January (winter), April (spring), and June (summer) 2009. In each season three samples were collected and analyzed for complex parameters. The sample location was chosen to represent a non-polluted area, without any industrial activity or habitants. After collection, samples were brought into the laboratory and filtered through a membrane filter paper (0.45 µm). A small fraction was kept in the refrigerator for further metal analysis. Sample pH, salinity, and conductivity were measured in the field as well as in the laboratory.

### Chemicals and Glassware

All the glassware used for experiments was pre-socked with 10% nitric acid (analytical grade) overnight and cleaned with ultrapure water (Millipore Milli-Q system). For pH adjustments, Merck suprapure NaOH and Merck suprapure HNO<sub>3</sub> were used. All other chemicals were of analytical grade and all solutions were prepared using ultrapure water (Millipore Milli-Q system).

### Instrumentation

Differential pulse anodic stripping voltammetry (DPASV) experiments were carried out with Metrohm Herisau Autolab, equipped with a 663 VA stand. Hanging mercury drop electrode (HMDE) was used as a working electrode whereas Ag/AgCl and graphite electrodes were used as a reference and auxiliary electrode respectively. All the experiments were done in the deposition step at potential -0.9 V (solution stirred with a rotating bar at 1500 rot min<sup>-1</sup>), deposition time 60 s, and rest time 30 s. Stripping was performed with 50 mV of

pulse amplitude, by scanning the potential from -0.7 V to -0.25 V at 5mVs<sup>-1</sup>. Total lead concentrations were measured after acid digestion using DPASV. To check organic adsorption onto the electrode, alternating current (ac) voltammetry was performed with a frequency of 50 Hz, signal amplitude of 10 mV, and phase angle of 90°.

Titration of filtrated samples with Pb<sup>2+</sup> followed by DPASV were carried out in a room at a controlled temperature (25°C) and dissolved oxygen was removed by bubbling 99.995% purity nitrogen.

Dissolved organic carbon (DOC) was analyzed with a Dohrmann DC-190 equipped with an infrared detector and determined in the form of CO<sub>2</sub> after decomposition of the sample in the furnace at about 6008°C.

### Complexing Parameters

Speciation parameters were calculated from the potential-current curves obtained along the Pb<sup>2+</sup> titrations. Experimental values of peak current (*i<sub>p</sub>*) and peak potential (*E<sub>p</sub>*) versus total Pb<sup>2+</sup> concentration added during the water sample titrations were fitted to theoretical curves based on labile complexes, according to the procedure described in our previous papers (Praveen et al. 2016).

## RESULTS AND DISCUSSION

Adsorption of organic matter on the Hg electrode will influence significantly speciation parameters determined from voltammetric titrations. To evaluate organic adsorption on the Hg electrode, changes on the double layer capacitance at the electrode surface with the applied potential were measured for the water samples collected and compared with those of the electrolyte solution. For the deposition potential used in DPASV measurements (-0.9 V) no organic adsorption was detected.

### Description of Water Quality Parameters

Water quality parameters such as pH, temperature, salinity, DOC, and total lead concentrations in different seasons are shown in Table 1. The value of pH varied from 7.34 to 7.56 and did not show any seasonal pattern. The highest pH value (7.56) was found in January and the lowest (7.34) in April. The temperature was lower in winter and gradually increased up to summer as expected. Salinity also showed a similar trend, increasing from winter (29.6) to summer (35.3), due to higher evaporation with the increase of temperature and decrease of the Tagus river flow in that period. DOC concentration is lower in summer (4.7 ppm) than in winter or spring (6 ppm). Total lead concentration varied from 2.5 nM (winter) to 16.90 nM (summer), both values lower than the

Table 1: Water sample characterization during the studied period.

Sample parameters	January (winter)	April (spring)	June (summer)
pH	7.56	7.34	7.46
Salinity (‰)	29.6	31.9	35.3
DOC (ppm)	6.0 ± 0.6	6.0 ± 0.7	4.7 ± 0.2
Water Temperature (°C)	10.6	15.4	19.1
Total lead (nM)	2.50 ± 0.62	9.94 ± 2.31	16.90 ± 4.35

one reported a decade before (Lindim et al. 2000), probably due to the river trace metal depuration in recent years.

### Lead Speciation in Different Seasons

The voltammograms of water samples in all seasons showed a shift to more negative peak potential ( $E_p$ ) values and a decrease in peak current ( $i_p$ ) values when compared to the calibration plot (Figs. 1A to 1C). In all experiments, along the titration with  $Pb^{2+}$ ,  $E_p$  tends to a more positive value as expected, since the complexing sites gradually saturate

decreasing the complexing strength. On the other hand, the  $i_p$  curve became parallel to the calibration plot because complexing sites are no longer in excess compared to the metal ion concentration. This behavior is commonly observed in estuarine waters (Lindim et al. 2000, Holly et al. 2017).

Table 2 shows the complexing parameters obtained from the best fitting between experimental and theoretical curves of peak current and peak potential along the titration with  $Pb^{2+}$  (Fig. 1A to 1C). Voltammetric data was interpreted assuming a macromolecular heterogeneous ligand of humic matter type, simply described by two types of binding sites with concentrations  $C_{L1}$  (minor sites with a stronger binding strength) and  $C_{L2}$  (major sites with a weaker binding strength). The diffusion coefficient  $D_{ML}$  of the macromolecular ligand was obtained from the first points of the titration curve where the mean diffusion coefficient of the labile species presented a near constant value equal to  $D_{ML}$  (Lindim et al. 2000, Mota et al. 2005).

From Table 2 it can be seen that both  $C_{L1}$  and  $C_{L2}$  sites of the macromolecular ligand presented the highest

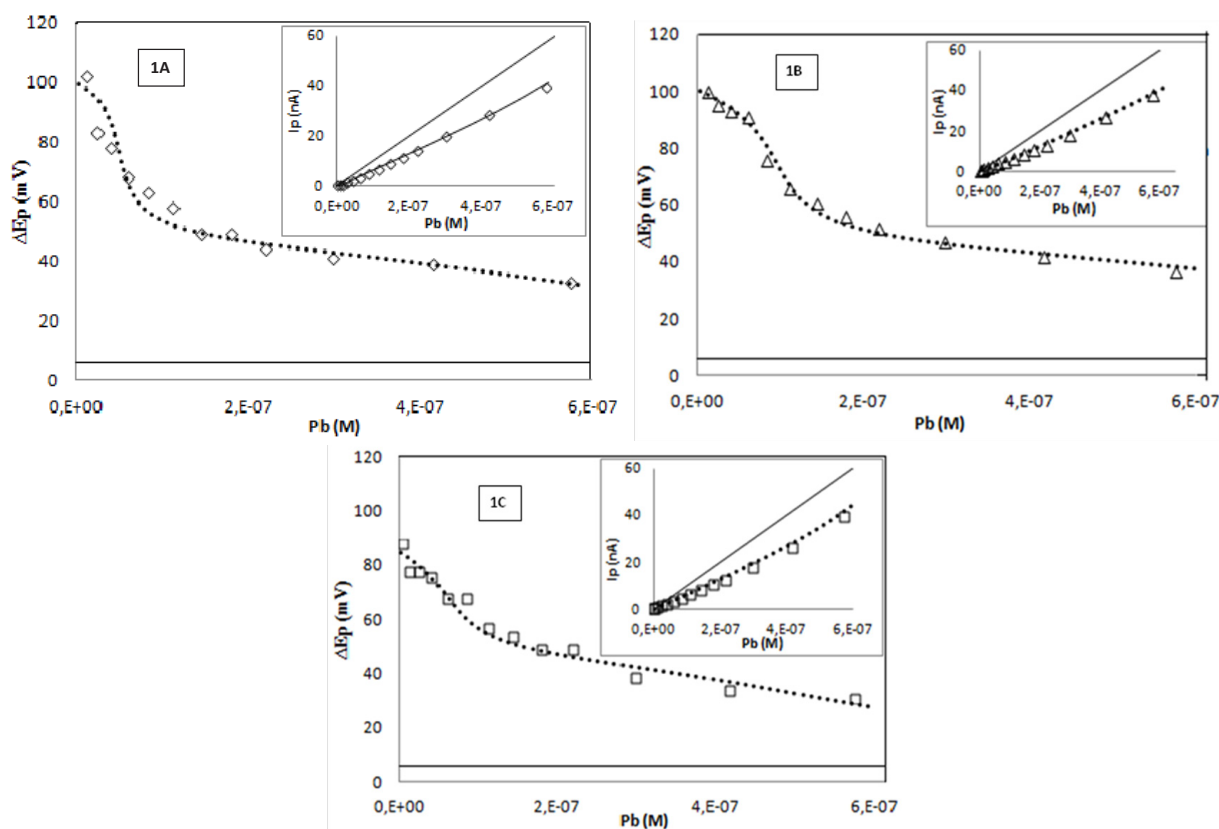


Fig. 1:  $\Delta E_p$  (shift of the peak potential) and  $i_p$  (peak current in inserted figure) versus added lead concentration. (---) - theoretical fitting curve. ( $\diamond$ ), ( $\Delta$ ), ( $\square$ ) - experimental values. Figs 1A, 1B, and 1C are samples collected in January, April and June respectively.

Table 2: Ligand complexing parameters during the studied period.

Complexing parameters	January	April	June
$D_{ML}$ ( $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ )	$3.11 \pm 0.26$	$3.11 \pm 0.26$	$3.11 \pm 0.26$
$C_{L1}$ ( $10^{-6} \text{ M}$ )	$1.20 \pm 0.1$	$2.25 \pm 0.2$	$1.52 \pm 0.2$
$K_{L1}$	$9.49 \pm 1.00$	$9.24 \pm 1.33$	$8.89 \pm 2.13$
$C_{L2}$ ( $10^{-6} \text{ M}$ )	$14.40 \pm 1.0$	$19.40 \pm 2.1$	$12.20 \pm 1.1$
$K_{L2}$	$6.56 \pm 1.1$	$6.39 \pm 0.4$	$6.63 \pm 1.0$

concentration in spring, which may be due to the bloom of phytoplankton activity in that season. Between spring and summer, a decrease of  $35 \pm 3\%$  in the concentration of all different sites ( $C_{L1}$  and  $C_{L2}$ ) was determined, which may be related to the decrease of DOC in the summer.

The decrease of stability parameter ( $K_{L1}$ ) from January to June (Table 2) is probably due to the salinity increase, which increases the competition of major cations (such as  $\text{Ca}^{2+}$ ) for the complexing binding sites. This competition depends not only on the affinity of the cation for the binding site but also on the concentrations of the species involved, decreasing with the increase of ligand concentration. The increase of salinity may also contribute to the decrease of stability parameter ( $K_{L2}$ ) parameter from winter to spring, but to explain the increase of  $K_{L2}$  from spring to summer other factors should be looked for. In fact, the pH shift (7.34 in April to 7.46 in June) may lead to an increase of  $K_{L2}$  since the de-protonation of  $C_{L2}$  with the increase of pH favors  $\text{Pb}^{2+}$  complexation. It should be noticed that the decrease of pH from winter to spring also favors the  $K_{L2}$  decrease observed from January to April. The small seasonal variations in pH and salinity did not significantly affect  $K_B$  due to the much larger concentration of B sites in solution.

## CONCLUSIONS

From lead speciation results obtained during the study period no systematic seasonal variation was observed for all the sites detected ( $C_{L1}$  and  $C_{L2}$  sites). However punctual trends observed in the concentration and stability parameters of certain sites could be explained from the variation of water parameters (e.g., salinity, pH, DOC), affected by the time of the year. The increase of salinity from winter to summer may contribute to the decrease of the  $C_{L1}$  (minor sites) stability parameter due to the competition of major cations. The seasonal variation of  $K_{L2}$  followed the trend of pH, increasing with de-protonation of  $C_{L2}$ . The decrease of DOC from spring to summer may explain the decrease in the concentration of all different sites present in solution and the phytoplankton bloom in the spring may be responsible for the higher concentration of  $C_{L1}$  and  $C_{L2}$  sites in April. To have a more complete picture, factors such as sedimentation, input fluxes and estuarine dynamic have to be included.

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