Spatiotemporal differences in trace element levels at Douro River and Ave River (Portugal) lower basins

Couto C.M.C.M.[1,2*], Ribeiro C.[1], Maia A.[1,4], Santos M.[1], Tiritan M.E.[1,5,6], Ribeiro A.R.[1,3], Pinto E.[2], And Almeida A.[2]

[1]CESPU, Instituto de Investigação e Formação Avançada em Ciências e Tecnologias da Saúde, Rua Central de Gandra, 1317, 4585-116 Gandra PRD, Portugal

[2]LAQV / REQUIMTE, Departamento de Ciências Químicas, Laboratório de Química Aplicada, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal

[3]*Present affiliation:* Laboratório de Processos de Separação e Reacção – Laboratório de Catálise e Materiais (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[4]Universidade Católica Portuguesa, CBQF – Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Arquiteto Lobão Vital, Apartado 2511, 4202-401 Porto, Portugal

[5]Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal

[6]Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR/CIMAR), Universidade do Porto, Rua dos Bragas, 289, 4050-123 Porto, Portugal

*corresponding author: Cristina M.C.M. Couto.

e-mail: cristina.couto@iucs.cespu.pt

Abstract Douro and Ave lower basin water quality was studied regarding a wide panel of trace elements (Li, Be, Al, Ti, V, Cr, Co, Ni, Cu, Zn, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th and U). To take into account expected spatiotemporal changes and to look for anthropogenic sources of contamination, samples were collected at different sampling sites (9 in Douro; 5 in Ave) in three sampling campaigns.

According to widely accepted water quality guidelines for the protection of aquatic life, trace elements mean values were found high for Al, Cu, Se, Ag, Cd and Pb in both Douro and Ave, plus Zn in Ave.

Significant spatial differences were found, especially in Ave, where a noticeable trend for higher values from upstream to downstream was observed for several elements. Seasonal differences were also observed, with higher levels in spring for most elements, especially in Douro.

Keywords: Douro and Ave lower basin, river water, environmental monitoring, trace elements, ICP-MS

1. Introduction

Rivers water quality can be used as an indicator of the pollution load on the environmental surroundings, especially in urban estuaries (Chapman, 1996). The composition of surface waters is dependent on natural factors (geological, topographical, meteorological, hydrological and biological) in the drainage basin and varies with seasonal changes in runoff volumes, weather conditions and water levels (Bartram and Balance, 1996). Human intervention also has significant effects on surface water quality. Some of these effects are the result of hydrological changes (building of dams, draining of wetlands and diversion of flow) or polluting activities, such as the discharge of domestic, industrial, urban and other wastewaters into the watercourse (Bartram and Balance, 1996). Among the main inorganic pollutants usually found in estuarine waters, metals are of particular concern due to their potential toxic effects and ability for bioaccumulation. Heavy metals contamination may have devastating effects on the ecological balance of the recipient environment and on the diversity of aquatic organisms (Baby *et al.*, 2010).

Despite the economic and social importance of Douro and Ave rivers basin in North Portugal, few works exist on the characterization of metallic pollutants and its bioaccumulation. The Douro and Ave estuarine water and sediments have been reported to be contaminated by trace metals and some studies showed a clear signature of anthropogenic contamination, with metals levels indicating potential toxicity for sediment biota (Couto *et al.*, 2014; Magalhães *et al.*, 2007; Mucha *et al.*, 2003; 2004; 2005; Soares *et al.*, 1999; Alves *et al.*, 2009).

Both rivers have nature reserve areas at their mouths – the Nature Reserve of the River Douro Estuary (Douro) and the Ornithological Reserve of Mindelo (Ave) – both being the birth nest of numerous species and regularly hosting birds (kingfishers, herons, common sandpipers, ruddy turnstones, knots, bluethroats, gulls, etc.) during their annual migration between Europe and Africa.

The aim of this work was to perform a comprehensive spatiotemporal study on the trace element levels of both river basins. The main goals were (1) to determine the

levels of a large panel of relevant trace elements (metals, semi-metals and non-metals) in both estuarine waters; (2) to evaluate the spatial and seasonal changes in trace element levels; and (3) to evaluate the spatial differences in trace element levels along the basins in order to detect potential inputs (sources of contamination).

2. Experimental

2.1. Study area

Douro is the second most important river in Portugal. From its 927 km of total extension, 208 km are in Portuguese territory, where it flows into the Atlantic Ocean. Its lower basin is 22 km long. The last 8 km of the basin (Figure 1A) are located between the cities of Porto (north bank) and Vila Nova de Gaia (south bank), in a heavily populated region, with over 700,000 inhabitants – the Porto Metropolitan Area (PMA), the second largest Portuguese metropolitan area. This lower part of the basin receives largely untreated sewage from inhabitants of PMA and the discharges of a total of eight wastewater treatment plants (WWTP) (Azevedo *et al.*, 2006). The two main WWTP discharge a mean sewage flow of about 94,000 m^3/day.

For this study, nine sampling sites (SS1 to SS9) were selected from the river mouth, near the Atlantic Ocean, to the Crestuma-Lever dam (Figure 1A). Sampling sites SS1, SS2, SS6 and SS9 were located on the north bank of the river, whereas SS3 (Nature Reserve of the River Douro Estuary), SS4, SS5, SS7 and SS8 were located at the south bank, bordering the other highly industrialized and densely inhabited city, Vila Nova de Gaia.

The Ave basin is located on the northwest of Portugal, and has an area of about 458 km^2. Ave main watercourse has 101 km of total extension. It has a drainage area of 1340 km^2, with a mean annual freshwater flow of about 40 m/s. Its most important tributaries are the Este and Vizela rivers, which significantly contribute to the total freshwater flow of the Ave. Most of the river basin surrounding area is used for agriculture practices (vines, fruits and cereals), forest and pasture fields. This river basin is also exposed to multiple discharges of wastewater, without previous treatment, due to strong textile, leather tannery and rubber industrial activity.

Ave estuary mouth (Figure 1B) is located at the city of Vila do Conde, where a fishery harbor and a shipyard exist. As mentioned above, at this last part of the river, an important natural ornithological reserve exists (sampling point SS1). A total of five sampling sites were selected along the estuary. SS2, SS4 and SS5 were located on the north bank of the river whereas SS1 and SS3 were located at the opposite bank.

Figure 1. Map of the Douro estuary (A) with the location of the nine sampling sites (SS1 to SS9) and Ave estuary (B) with the location of the five sampling sites (SS1 to SS5).

2.2. Sample collection and preparation

Samples were collected during low tide in spring (May 2013), summer (August 2013) and autumn (November 2013). Standard water sampling procedures (Eaton *et al.*, 2005) were used to collect the samples. During transport, samples were kept refrigerated (±4 ºC), in the dark. At the laboratory they were immediately vacuum filtered through 1.2 µm glass fiber filters and acidified to pH 2 with ultrapure concentrated (65% w/w) nitric acid.

2.3. Trace element analysis

Trace element determination was performed using a VG Elemental (Winsford, UK), PlasmaQuad 3 ICP-MS. Analytical procedure was based on the U.S. Environmental Protection Agency (EPA) Method 200.8 "Determination of trace elements in waters and wastes by inductively coupled plasma - mass spectrometry" (Creed *et al.*, 1994). The analytical masses (m/z ratios) monitored and the detection limits achieved are indicated in Table 1. Besides the trace elements within the scope of application of EPA 200.8 method, several other elements were analyzed, some in the ICP-MS semi-quantification mode. Results for Br, Sn, Cs, La and Ce were also considered in the statistical analysis. Before each analytical run the instrument was tuned for maximum signal sensitivity and stability using ^{115}In as the target isotope. All samples were analyzed in duplicate (two determinations in the same analytical run) after a single 1+1 dilution with internal standard solution (40 ppb of Sc, Y, In, Tb and Bi).

Instrumental limits of detection (LoD) were calculated as the concentration corresponding to 3 times the standard deviation of 10 repeated determinations of the calibration blank signal (Table 1). For mathematical calculations,

results below the LoD were imputed as the LoD divided by the square root of 2 (Hornung and Reed, 1990).

3. Results and Discussion

A summary of the results obtained for the set of 20 elements determined is presented in Table 1. According to the whole dataset (mean values for all the sampling sites and the 3 sampling campaigns), the order of abundance in Douro water was: Al > Li > Ti > Ba > Zn > V ≈ Mo ≈ Cu > Pb > Cr > Ni > Se > U > Sb > Ag > Co > Th ≈ Tl ≈ Cd > Be. In Ave water samples the order was: Al > Zn > Se > Mo > Li > V > Ba > Ti ≈ Cu > Pb > Ni > Cr > U > Be > Co ≈ Sb > Ag ≈ Cd > Tl ≈ Th.

Mean values for trace element concentrations were found above aquatic life limits (CCME 2017) for Al, Cu, Se, Ag, Cd and Pb in both estuaries, plus Zn in Ave estuary. SS1 in Ave estuary presented the highest values for almost all the trace elements determined.

Table 1. Results (ppb) for the trace element determination in Douro and Ave rivers lower basin water samples collected at 9 (Douro) and 5 (Ave) sampling sites in three seasons (n = 42).

	Douro		**Ave**		**Aquatic life limit[#]**
Element	**Mean***	**Range**	**Mean***	**Range**	
Li	28.4	1.9 - 99.6	27.1	0.84 - 75.2	--
Be	0.033 *(n=20)*	0.002 - 0.2	2.07	0.002 - 8.51	--
Al	240.2	1.26 - 2718	1932	4.45 - 9021	100
Ti	23.4	0.41 - 118.5	21.9	1.26 - 76.2	--
V	13.9	0.50 - 42.1	24.1	0.68 - 72.1	--
Cr	6.23	0.19 - 97.0	4.1	0.90 - 10.9	1
Co	0.71	0.13 - 2.52	1.19	0.16 - 3.74	--
Ni	6.83	0.84 - 30.5	7.5	1.27 - 16.3	95.6**
Cu	13.2	0.97 - 64.6	21.7	2.6 - 97.8	2.4**
Zn	14.2	2.97 - 57.5	48.6	9.65 - 227	30
Se	5.26 *(n=23)*	0.04 - 60.1	32.6 *(n=38)*	0.041 - 147.6	1
Mo	13.7	0.11 - 38	29.6	0.085 - 122.8	73
Ag	0.91	0.024 - 6.5	0.64	0.007 - 3.84	0.25**
Cd	0.11	0.016 - 0.304	0.62	0.021 - 2.51	0.09
Sb	1.3	0.043 - 24.6	1.2	0.149 - 2.64	--
Ba	19.7	6.2 - 31.6	23	7.47 - 65.7	--
Tl	0.12	0.005 - 1.85	0.25	0.018 - 0.804	0.8
Pb	10.1 *(n=41)*	0.061 - 85.4	10.7	0.123 - 81	3.2**
Th	0.17 *(n=41)*	0.004 - 0.99	0.21	0.002 - 0.442	
U	2.0	0.32 - 3.68	2.3	0.133 - 6.53	15

*The number inside the parenthesis indicates the number of samples with > LoD result. For mathematical calculations, values < LoD were imputed as LoD /√2). [#] According to Water Quality Guidelines for the Protection of Aquatic Life (Canadian Environmental Quality Guidelines, from the Canadian Council of Ministers of the Environment) (CCME, 2017). ** for maximum hardness 100 mg/L $CaCO_3$.

LoD: 0.002 (^{7}**Li**); 0.002 (^{9}**Be**); 0.03 (^{27}**Al**); 0.124 (^{45}**Ti**); 0.008 (^{51}**V**); 0.077 (^{52}**Cr**); 0.002 (^{59}**Co**); 0.01 (^{60}**Ni**); 0.032 (^{65}**Cu**); 0.059 (^{66}**Zn**); 0.041 (^{82}**Se**); 0.027 (^{95}**Mo**); 0.002 (^{107}**Ag**); 0.011 (^{111}**Cd**); 0.003 (^{121}**Sb**); 0.016 (^{137}**Ba**); 0.003 (^{205}**Tl**); 0.002 (^{208}**Pb**); 0.001 (^{232}**Th**); 0.001 (^{238}**U**). Note: ^{81}Br, ^{118}Sn, ^{133}Cs, ^{139}La and ^{140}Ce (in the semi-quantification mode analysis) and ^{45}Sc, ^{89}Y, ^{115}In, ^{159}Tb and ^{209}Bi (as internal standards) were also monitored.

3.1. Spatial differences

Important spatial differences in trace elements levels were observed in both rivers course. Figure 2 highlights the main findings. To simplify, only the elements presenting a value higher than mean ± 2SD at any SS are displayed, in case of Douro (Figure 2a). Those elements were Al, Ti, Cr, Sn, Sb, Ba, Tl and Pb. The sampling sites SS3-SS5 showed the highest total metallic content. These sites are well within the cities of Porto and Vila Nova de Gaia. Lead was significantly higher at SS8, a sampling point located close to the dam, near a WWTP discharge.

For Ave, since almost all elements were significantly higher at SS1, mean values were calculated excluding this sampling site values ($mean_2$), and the same criterion was used to draw the Figure 2b. The elements presenting a value higher than $mean_2$ ± 2SD at any SS were Li, Be, V, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Ba, Ce, Tl, Pb, Th and U.

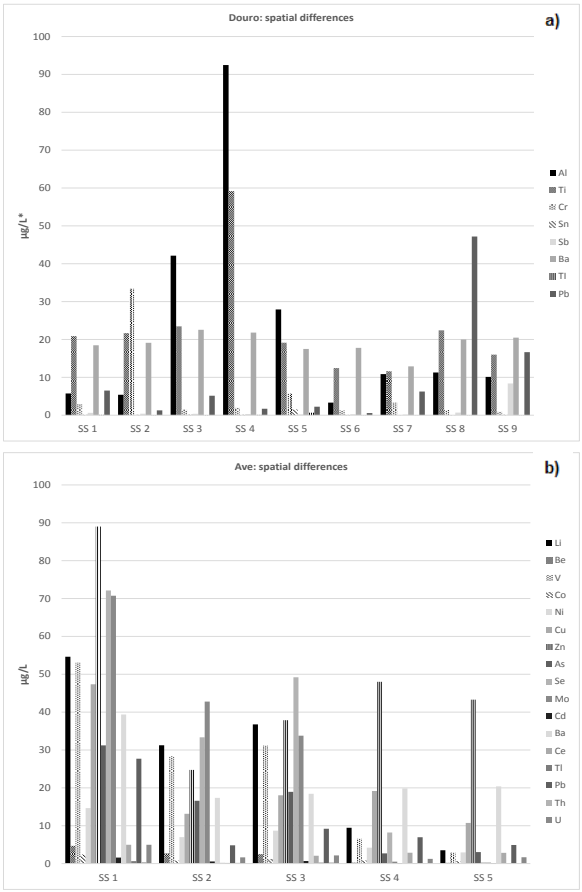

Figure 2 – Differences in trace element levels according to sampling site in Douro (a) and Ave (b) rivers. Results as mean values for the 3 seasons. (*Results for Al are x10). Only the elements showing a value higher than the mean ± 2SD at any sampling site (SS) are depicted. (Note: for Ave, $mean_2$ was calculated excluding SS1 values; see text for details).

In Ave, a clear tendency for lower values from downstream to upstream (accompanying the salinity values and reflecting the influence from seawater) was observed for several elements: Li, V, Ni, Se, Mo, Be, Cd, Tl, Th, Co, Br, and even, with some exception, for Ag (excluding SS4), Sn (excluding SS1), Sb (excluding SS5) and U (excluding SS5).

In Douro, where the sampling points were much further away from the mouth of the river, such downstream to upstream tendency for lower values was noticeable only for Li, V and Se.

3.2. Seasonal changes

Some important seasonal differences in trace elements levels were also observed. Figure 3a shows the elements presenting values out of mean ± SD interval at any season in Douro samples. (Al in spring and Br in summer also presented concentrations higher than mean ± SD; data not shown due to scale difficulties). Most elements (Ti, Cu, Zn, Mo, Sb, Ba, La, Ce and Pb and Al in Douro) presented higher values in spring. Seasonal differences were even more noticeable in Ave. Figure 3b shows the elements presenting values out of mean ± SD interval at any season. Again, besides the elements shown in the figure, Al in spring and Br in summer also were at concentrations higher than mean ± SD. Most elements (Be, Ti, Cr, Co, Cu, Zn, Mo, Ba, La, Ce and Pb) presented at higher values in spring. These seasonal changes in trace element levels in both rivers reflect their particular hydrodynamics changes with season and rainfall and the runoff or leach of the surrounding soils into river water.

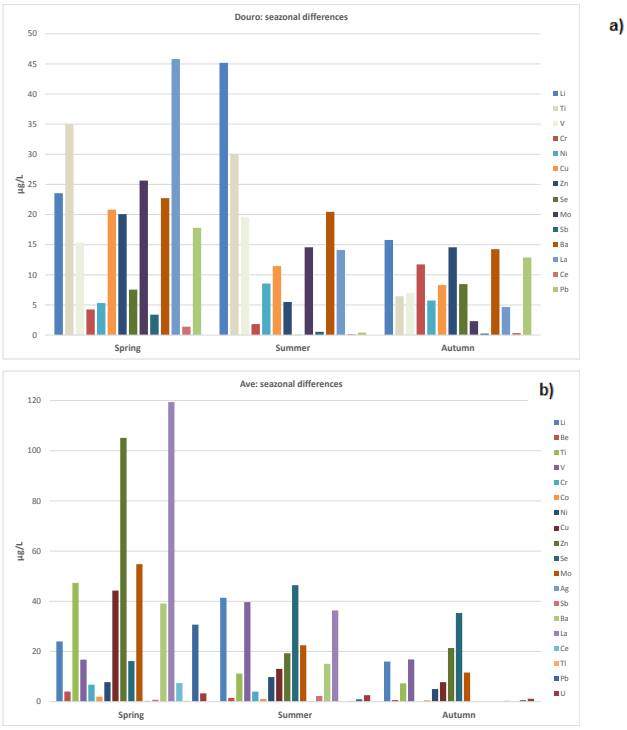

Figure 3 – Differences in trace element levels according to the season in Douro (a) and Ave (b) rivers. Results as mean values for the 9 SS in Douro and the 5 SS in Ave.

4. Conclusions

The Douro and Ave lower basin water was studied regarding trace element levels. The main conclusions can be summarized as follows:

- Most of the trace elements determined presented mean values lower than recommended aquatic life limits for long term exposure in freshwater. The exceptions were Al (240.2 and 1932 ppb), Cu (13.2 and 21.7 ppb), Se (5.26 and 32.6 ppb), Ag (0.91 and 0.64 ppb), Cd (0.11 and 0.62 ppb) and Pb (10.1 and 10.7 ppb) in Douro and Ave, respectively, and Zn (48.6 ppb) in Ave.

- Sampling site SS1 in Ave – a small lagoon located at the mouth of the river – showed a highly distinctive profile, with significantly higher levels of all trace elements.

- Several trace elements showed a clear tendency for higher levels from upstream to downstream. This may be a consequence of increased inputs along the basin and/or sediment resuspension, but especially the result of seawater influence. It was particularly noticeable in Ave lower basin, where sampling sites were much closer to the river mouth.

- Important seasonal differences in trace element levels were also found.

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