Seasonal evolution of natural radionuclides in two rivers affected by acid mine drainage and phosphogypsum pollution

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Abstract

The Odiel and Tinto rivers show singular characteristics due to the significant acid mine drainage (AMD) generated in the first section of their basins and the phosphogypsum (PG) stacks located on their common estuary. AMD leads to low pH and high redox potential, which keep high amounts of toxic elements and radionuclides in dissolution. The objective of this work was to analyse the seasonal evolution of U-Th isotopes and ^{210}Po in these rivers and the estuarine mixing zone. Four sampling points were selected (a fluvial point and an estuarine one for each river) and water samples were collected monthly throughout a year. The concentrations of natural radionuclides in the dissolved and particulate phases were determined by alpha spectrometry. The Odiel and Tinto rivers show concentrations of U-Th isotopes and ^{210}Po from one to three orders of magnitude higher than background continental waters due to the strong effect of AMD, and ^{234}U/^{238}U activity ratios up to 2.

The studied radionuclides show a clear seasonal behaviour in these rivers, with three different stages during the year: 1) concentration peaks observed during November and December due to the "washing effect" produced by the first rainfalls of the hydrological year, 2) a "dilution effect" by runoff in the rainy winter, and 3) a progressive "concentration effect" during the spring and summer. A non-conservative behaviour of the analysed radionuclides in the estuaries was demonstrated due to precipitation processes produced by the increase of pH. The polluted outflows from the PG stacks located in the Tinto estuary produce a significant radioactive impact, mainly during the rainiest months, increasing the concentration of U-isotopes and ^{210}Po in the particulate phase.

Keywords

Natural radionuclides, acid mine drainage, phosphogypsum, non-conservative, water mixing

1. Introduction

The Tinto and Odiel rivers are located in southwest Spain in the province of Huelva. They present marine influence in their final reach, converging in the common Huelva estuary (Fig. 1). The Tinto River is 101 km long while the Odiel River is 140 km long, and their catchments cover 1600 and 2300 km^2, respectively. These rivers and their estuary have a great hydrochemical and environmental interest due to two factors. The first is the extensive acid mine drainage (AMD) affecting both rivers because of the existence of several old abandoned sulfide mines in their basins and second is the large chemical industrial complex and phosphogypsum (PG) stacks located by the Huelva estuary.

Regarding the AMD, these rivers drain one of the biggest metallogenic regions of massive sulfides in the world: the Iberian Pyritic Belt (IPB). Mining works date from the year 2500 B.C. in this region, although the large-scale exploitation of these deposits took place during the nineteenth and twentieth centuries (Leblanc et al., 2000). The sulfide deposits are predominately composed of pyrite (FeS_2, > 90% of volume), with variable amounts of sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and galena (PbS) (Sáez et al., 1999; Venkateswarlu et al., 2016). The exposure of these sulfides to oxygen and water liberates sulfate ions and metals and leads to acidity (pH = 2.5-3.0), polluting the waters (Cánovas et al, 2007). There are few works worldwide about concentrations and behaviour of natural radionuclides in locations affected by AMD, but high activity concentrations in these polluted environments have been found mainly for U-isotopes (Fernandes et al., 1998; Yamamoto et al., 2010; Durand, 2012; Madzivire, et al., 2014). In the study area some previous works also shown large concentrations of natural radionuclides with enhanced contents of U-Th isotopes and ^{210}Po in both waters and sediments (Hierro et al., 2012, Hierro et al., 2013, Blasco et al., 2016, Manjón et al., 2019a).

The AMD conferss extreme physicochemical conditions on these rivers, which maintain high concentrations of toxic elements in solution (Cánovas et al., 2007; Nieto et al., 2007; Hierro et al., 2014) and radionuclides (Hierro et al., 2013). When these pollutants arrive at the Huelva estuary, they produce a severe environmental impact (Vicente-Martorell et al., 2009; Cánovas et al., 2010; Sánchez-Moyano et al., 2010). The differences between the physicochemical parameters of the marine and fluvial waters produce a strong pH gradient in the estuarine mixing zone due to the neutralization of these acidic waters and the precipitation of heavy metals and other pollutants from the dissolved into the particulate phase (Achterberg et al., 2003; Braungardt et al., 2003; Hierro et al., 2013, 2014). It is important to take into account that this mixing process does not occur at a steady point. A spatial displacement has been demonstrated, and while

during the dry seasons the mixing takes place in the most internal zones of the estuary, during the wet seasons this process takes place in sectors closer to the coast (Carro et al., 2011).

The five phosphoric acid plants included in the chemical industrial complex located on the Huelva estuary generated around 100 Mt of a waste called phosphogypsum (PG) between 1968 and 2010, which is stored in large piles on the salt-marshes of the Tinto River covering an area about 1000 ha (Fig. 1). PG is generated during the production of phosphoric acid, and is essentially composed of gypsum ($CaSO_4 \cdot 2H_2O$) but contains high concentrations of ^{238}U series natural radionuclides and other impurities such as P_2O_5 (pH ≈ 1.5), F, and toxic metals (Pérez-López et al., 2007; Bolívar et al., 2009). The high concentration of natural radionuclides of PG comes from the raw material used in the industrial process, which in the case of Huelva was sedimentary phosphate rock from Morocco (Bolívar et al., 1996). This phosphate rock contains U-series radionuclide concentrations of around 1500 Bq kg^{-1} (≈ 50 times higher than unperturbed soils), with ^{238}U in radioactive equilibrium with its daughters. About 20% of the U, more than 70% of the Th, and the majority of the Ra, Pb and Po (> 95%) contained in the phosphate rock remain in the PG after the industrial process (Bolívar et al., 1996; Bolívar et al., 2009). Therefore, PG is currently considered a Naturally Occurring Radioactive Material (NORM) (IAEA, 2003; Directive 2013/59/Euratom). On the other hand, the remaining phosphoric acid trapped between the PG particles explains the high acidity and polluting potential of the aqueous leachates produced by this waste (Pérez-López et al., 2010; Pérez-Moreno et al., 2018).

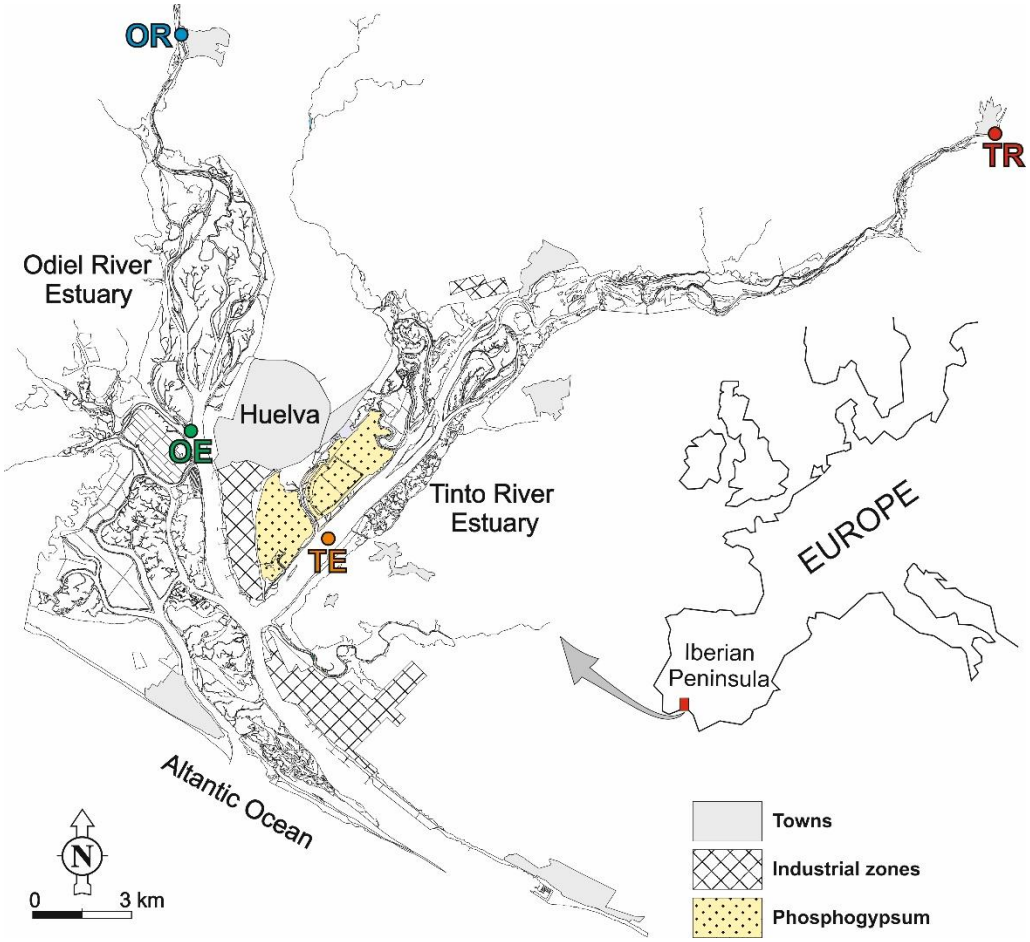

Figure 1. Map of the study area showing the sampling points: Odiel River (OR), Odiel Estuary (OE), Tinto River (TR), and Tinto Estuary (TE).

Until 1998, about 20% of the generated PG was discharged into the Odiel River channel, while the remaining 80% was pumped in suspension with seawater into the stacks, where PG was decanted, and the polluted acidic (pH ≈ 2) seawater (around 10^7 m^3 $year^{-1}$) was released into the Tinto River channel without any treatment (Bolívar et al., 2000). From 1998 until the end of the production (31 December 2010), due to a change in the environmental policy according to the OSPAR convention (OSPAR, 2002, 2007), all the PG was pumped with fresh water in a closed circuit and placed into the piles, which reached around 30 m in height in some sectors. The northern and southern areas of the stacks (around 550 ha) have been partially restored (Más et al., 2006). Nevertheless, there are several points were the acidic polluted waters from the PG piles (restored and unrestored) are reaching the waters of the Tinto estuary (Pérez-López et al., 2015, 2016; Papaslioti et al., 2018).

Considering these facts, the aim of this work is to study the concentrations and behaviour of U-Th isotopes and ^{210}Po during a year in the acidic mining waters of these rivers and their polluted estuaries.

2. Material and methods

89 For this study, four sampling points were selected: OR and TR are located in the Odiel and Tinto rivers, while OE and
90 TE are located in the Odiel and Tinto estuaries, respectively. OR and TR represent fluvial composition without any
91 marine influence. At these four points, water samples were collected monthly throughout a year (from October 2009 to
92 September 2010). In total, 48 water samples of 10 L each were collected. Temperature, pH, electrical conductivity (EC)
93 and redox potential (Eh) were measured *in situ* using a Crison MM40+ portable multimeter, with a 5048 (Ag/AgCl)
94 electrode. The instruments were calibrated before sampling, and the redox potential was corrected to obtain the potential
95 relative to the hydrogen electrode (Eh) according to Nordstrom and Wilde (1998).
96 Water samples were filtered in the laboratory by using polycarbonate filters 9.0 cm in diameter with a pore size of 0.45
97 μm. Concentrated HNO_3 was added to achieve pH < 2 in order to prevent the adsorption of radionuclides onto the
98 container walls. The filters were dried and weighed, and the particulate matter (PM) content was calculated by
99 subtracting the filter mass. The filters were cleaned with HNO_3, and the liberated particulate matter was dissolved by
100 applying atmospheric acid digestion with aqua regia (3 HCl:1 HNO_3). The dry residue was re-dissolved in 8 M HNO_3.
101 Major and minor elements were determined in the dissolved matter by Inductively Coupled Plasma Optical Emission
102 Spectroscopy (ICP-OES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) at Actlabs (Canada). The
103 quality control (QC) was developed by the measurement of Certified Reference Materials (CRMs) and a duplicate every
104 ten samples.
105 Radionuclides in dissolved and particulate matter were determined by a sequential extraction technique based on the
106 use of tributylphosphate (TBP) (Bolívar et al., 2000), subsequent electrodeposition onto a stainless-steel disc (U-Th
107 isotopes) and selfdeposition onto a silver disc (^{210}Po), and measurement of the activities by α-spectrometry using ion-
108 implanted silicon detectors (Bolivar et al., 2000) with 25% absolute efficiency. The QC for alpha-particle measurements
109 was conducted by participating in annual international proficiency tests (International Atomic Energy Agency [IAEA]
110 and the Spanish Nuclear Safety Council [CSN]), and by measuring both a blank and CRMs for every set of six samples
111 (IAEA-443).

112 **3. Results and discussion**

113 **3.1 Fluvial discharges**

114 Rainfall in the province of Huelva is very irregular, with high intra- and interannual variability. This irregularity in the
115 precipitation together with the low permeability of the Tinto and Odiel river basins explains the large variations in the
116 flow of these rivers (Olías et al., 2006). The rainfall is concentrated throughout the wet season, between the months of
117 October and April, preceded by the low flow-season between the months of May and September. The average annual

flows of the Odiel and Tinto rivers are 29 and 1.6 $m^3 s^{-1}$ respectively (Olías et al., 2006), but the flows can increase by up to two orders of magnitude during floods, mainly in the autumn and winter months.

The average rainfall recorded during the study period at meteorological stations located close to the fluvial sampling points (OR and TR) was very high (960 mm) compared to the average rainfall in the area (550 mm). The highest precipitations were registered in the winter months, with occasional rain during the spring and very low rainfall during the summer and autumn months (Fig. S1 of the supplementary material). Figure 2 shows the Odiel River flow data recorded in the stream gauging station close to the OR sampling point (unfortunately, there are no data for the Tinto River flow). It should be noted that during the autumn there was no flow in the Odiel River, which is unusual since November is normally one of the rainiest months. The highest flows, like the precipitations, were recorded during the winter months with a maximum in February (1755 $m^3 s^{-1}$).

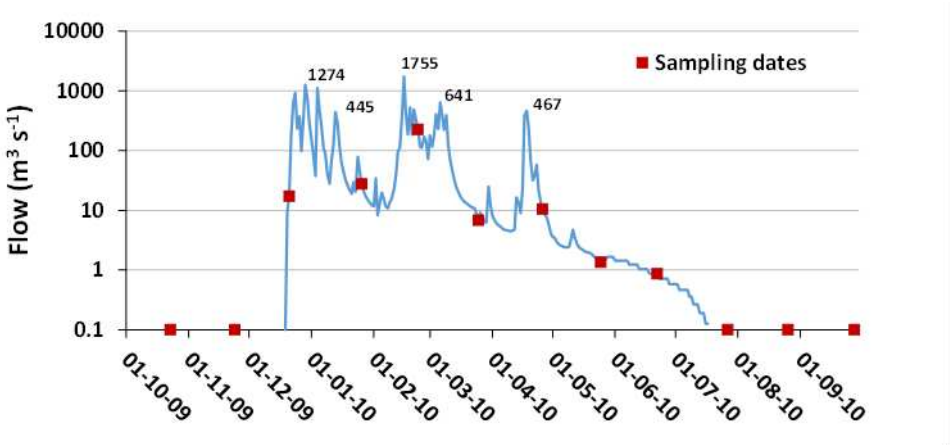

Figure 2. Daily flow of the Odiel River during the study period indicating the sampling dates

3.2 Hydrochemistry

The measured physicochemical characteristics are in Table S1 of the supplementary material. The pH of the Odiel and Tinto rivers shows the acidity of their waters during the year, with median pH values of 3.2 and 2.7, respectively. The lower pH in the Tinto River is due to the greater impact produced by the AMD on its course (Olías et al., 2004). In both estuaries, the pH values are very similar and notably higher than the fluvial ones, with almost neutral mean values (OE = 7.0, TE = 6.9) due to the influence of the seawater (pH ≈ 8). Regarding the temporal evolution (Fig. 3A), the behaviour of the pH at the estuarine points (OE and TE) is opposite to that in the rivers (OR and TR). This is explained by the fact that the intense rain decreases the acidity of the rivers during the winter and spring months due to the dilution effect by runoff. On the other hand, the large discharge of fluvial water during these months (mainly January and February) displaces the seawater out of the estuaries, making the marine influence less important and increasing the acidity of their waters (Fig. 3A).

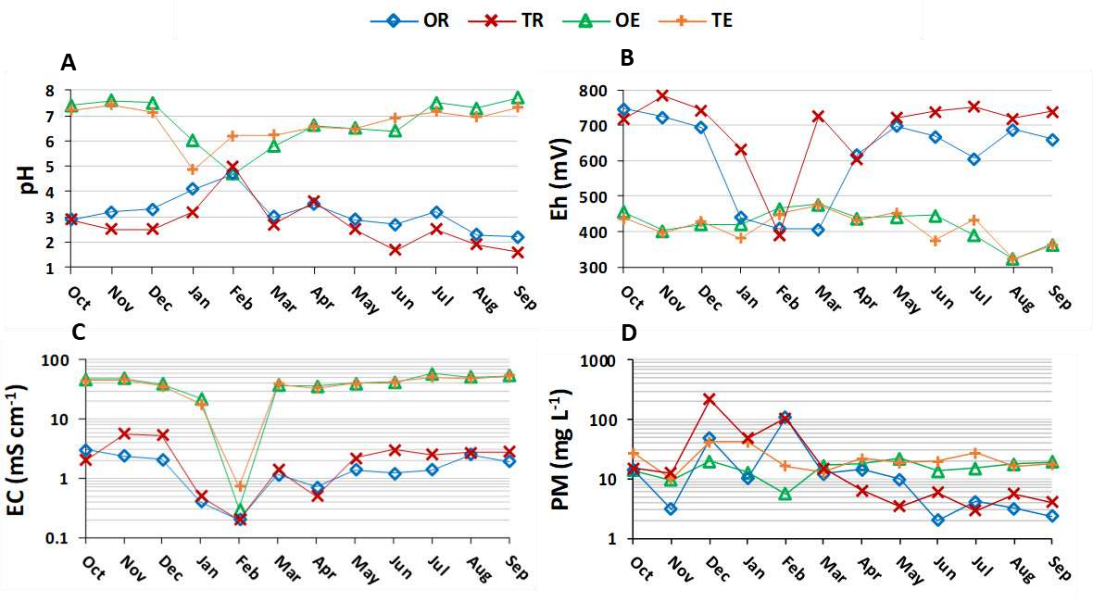

Figure 3. Evolution of pH (A), redox potential (B), electrical conductivity (C) and particulate matter (D) during the year in the riverine and estuarine sampling points.

The Eh showed the same mean value (≈ 420 mV) in both estuaries, similar to the value of seawater (400-435 mV) (Kennish, 2017), while in the rivers it is significantly higher (OR = 613 and TR = 689 mV) (Fig. 3B). Under these oxidising conditions, U is found primarily as U(VI) in the form of the highly soluble uranyl ion UO_2^{2+}, which forms complexes mainly with carbonate and phosphate under neutral conditions or with sulfate and fluorides at acidic pH values (Porcelli and Swarzenski, 2003), while under reducing conditions, uranium is predominantly present as U(IV) and tends to precipitate as insoluble minerals. In the rivers, the Eh decreased significantly during the winter months due to the dilution effect caused by rainfall, while in the estuaries it remained more or less constant during the year.

The mean values of EC in the fluvial waters were 1.5 and 2.4 mS cm^{-1} at the sampling points OE and TE, respectively, showing the large amount of dissolved ions transported by these rivers. The higher EC of the Tinto River is consistent with its higher acidity. In the estuaries the mean EC was around 40 mS cm^{-1}, slightly lower than the typical EC of seawater (50 mS cm^{-1}), as expected due to the mixing. The temporal evolution of the EC (Figure 3C) shows a similar pattern to the pH, with a large decrease during the rainy season (around two orders of magnitude) due to the great intake of fluvial water, mainly in February.

The particulate matter (PM) showed similar concentrations at both estuarine points with a mean of 15 and 23 mg L^{-1} in the Odiel and Tinto estuaries, respectively. At fluvial sampling points the median concentration was around 10 mg L^{-1}, with significant higher values (> 100 mg L^{-1}) during the winter months in relation to flood events, which produce an increase in the water turbidity (Fig. 3D).

The concentrations of major and trace elements in the dissolved phase are listed in Tables S2-S5 of the supplementary material, showing the values at the sampling points. The high concentrations of sulfate and metals in these rivers are due to the effeets of AMD. The mean sulfate concentrations in the Odiel and Tinto rivers were 970 and 1550 mg L^{-1}, respectively. The metals and metalloids with the highest concentrations at the fluvial sampling points were the following (mean concentration in brackets): Al (OR = 58 and TR = 86 mg L^{-1}), Zn (OR = 15 and TR = 21 mg L^{-1}), Mn (OR = 11.9 and TR = 8.6 mg L^{-1}), Cu (OR= 5.3 and TR=18.9 mg L^{-1}) and Fe (OR = 7.5 and TR = 144 mg L^{-1}). All these elements decrease their concentrations in the rivers by around one order of magnitude after flood events (January, February, and April in this study) due to the dilution effect and increase their concentrations during the dry season (Tables S2 and S3). At the estuarine points, the compositions of the waters are clearly influenced by seawater and are very similar to one another. The measured species with higher concentrations and their mean values (in brackets, mg L^{-1}) are as follows: Na (OE = 7800 and TE = 7400), SO_4^{2-} (OE = 2200 and TE = 2100), Ca (OE = 300 and TE = 330), K (OE and TE = 330), and Sr (OE and TE = 5.4). Several metals (Al, Fe, Cr, Pb, Sn) showed concentrations below the DL during the year. Almost all metals increase their concentrations in the estuaries by around one order of magnitude during the rainiest months due to the higher fluvial flow, while the elements with higher concentrations in seawater notably decrease their concentrations during these periods (Tables S4 and S5). These concentrations and behaviour agree with previous studies (Olías et al., 2006; Cánovas 2007; Hierro et al., 2014).

In order to know the influence of the rivers on their estuaries during the year, the percentages of fluvial water in this mixing zone were determined based on the conservative behaviour of Na (Loder and Reichard, 1981; Gordeev and Lisitzin, 2014), according to:

$$\%\ \text{fluvial water} = \frac{[X_{Na}(E)] - X_{Na}(SW)}{[X_{Na}(R)] - X_{Na}(SW)} \cdot 100 \quad (1)$$

where $X_{Na}(E)$ and $X_{Na}(R)$ are the concentrations of Na at the estuarine and fluvial sampling points, respectively, and $X_{Na}(SW)$ is the approximate concentration of Na in seawater (10^4 mg L^{-1}). These percentages are displayed in Figure 4. The high percentage of fluvial water at the estuarine points during the rainy season is noteworthy, mainly after the flood events of January (49 and 62% in the Odiel and Tinto estuaries, respectively), February (≈ 99% in both estuaries) and April (37 and 44% in the Odiel and Tinto estuaries, respectively). These values demonstrate the similarity between these two systems and the fact that the mixing zone is not spatially steady during the year; on the contrary, during the wet season, the mixing process takes place towards more outward sectors.

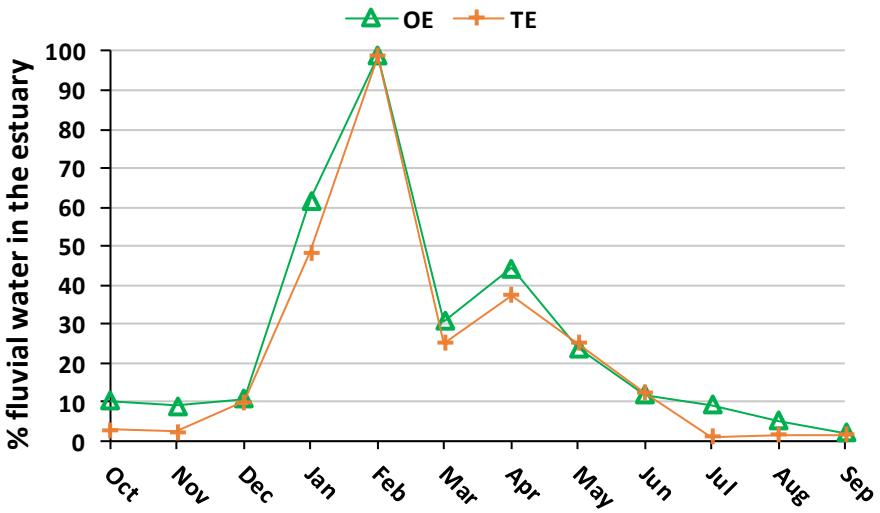

Figure 4. Percentage of river water in the estuarine sampling points.

3.3 Natural radionuclides

3.3.1 U-isotopes

The ^{238}U activity concentrations for the dissolved and particulate matter are displayed as box and whiskers plots in the Figure 5A, and the temporary evolution is shown in Figure 5B and C. Data are shown in Table S6 of the supplementary material. The mean concentrations in the dissolved phase were 49 and 57 mBq L^{-1} in the Odiel and Tinto rivers, respectively, approximately 10 times higher than the background values of continental surface waters in Europe (around 4 mBq L^{-1}) and worldwide (6 mBq L^{-1}) (De Vos and Tarvainen, 2006). In the estuaries, the dissolved ^{238}U activity concentrations are similar, with means of 33 and 36 mBq L^{-1} for the Odiel and Tinto estuaries, respectively (Fig. 5A), slightly lower than the mean for marine water (40 mBq L^{-1}; Ku et al., 1977). Nevertheless, concentrations higher than 50 mBq L^{-1} were reached, mainly in the Tinto estuary.

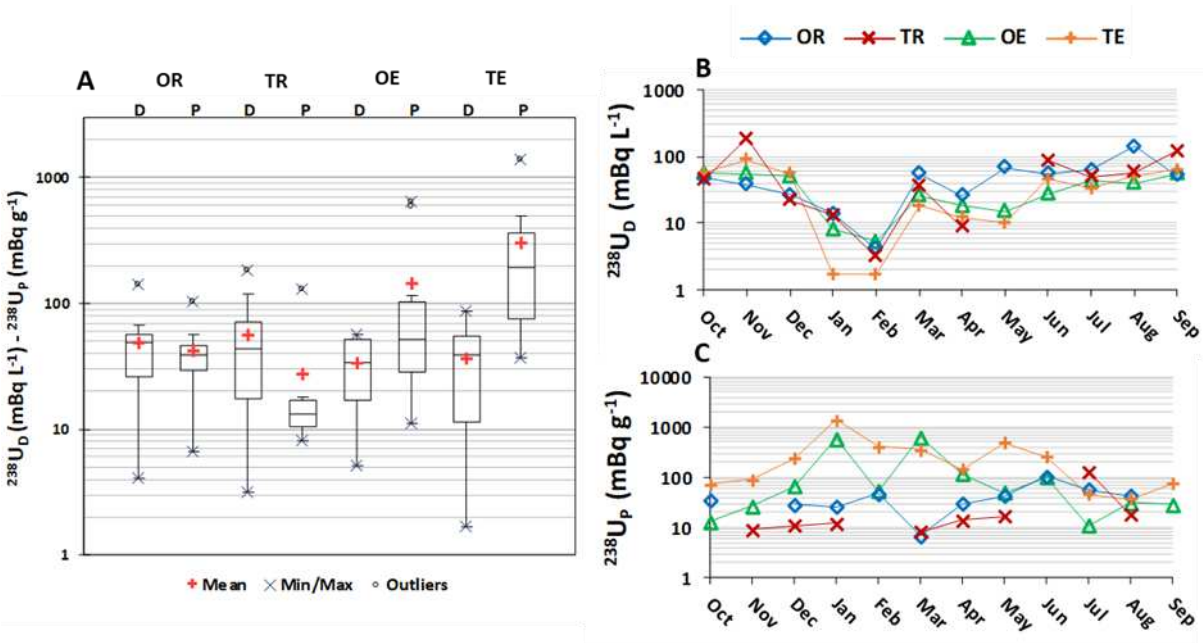

Figure 5. Box whisker plots of ^{238}U concentration in the dissolved and particulate phases (A), and temporal evolution for the dissolved (B) and particulate phases (C). Central line: median; box limits: first and third quartiles; whiskers: minimum and maximum non-outliers.

According to Figure 5B and taking into account the obtained uncertainties, which were lower than 10% (Table S6 of the supplementary material), the dissolved ^{238}U shows a clear seasonal pattern in both rivers and estuaries with an important decrease during the winter months because of the dilution effect during the rainy season. During the rainiest months, an additional U input in the Tinto estuary should be considered: the lateral polluted outflows from the PG stacks, which show a mean concentration of ^{238}U of $4.5 \cdot 10^4$ mBq L^{-1} (Pérez-Moreno et al., 2018), because of the surface runoff and groundwater. The dissolved activity concentrations increase progressively during the dry season at all the sampling points due to the decrease in the river flows (Figure 2). While the maximum concentration for the Odiel River was measured in the month of August (140 ± 4 mBq L^{-1}), the Tinto River reached its maximum in November (182 ± 13 mBq L^{-1}). This peak of dissolved ^{238}U in the Tinto River is related to the dissolution of the efflorescences precipitated during the dry season by the first rainfalls of the hydrological year (Cánovas et al., 2007).

In the particulate matter, the mean ^{238}U concentrations at the fluvial points were 42 and 27 mBq g^{-1} in the Odiel and Tinto rivers, respectively, while in the estuaries they were significantly higher, at 143 and 300 mBq g^{-1} in the Odiel and Tinto estuaries, respectively (Figure 5C). The ^{238}U concentration in the particulate matter of the estuaries is one order of magnitude higher than the worldwide median concentration in unperturbed sediments, which is 35 mBq g^{-1} with a range from 16 to 110 mBq g^{-1} (UNSCEAR, 2000). The high concentration of this radionuclide in the Tinto estuary is probably related with the releases from the PG stacks. The particulate ^{238}U activity concentration does not show a seasonal pattern as clearly as the dissolved one. The highest activity concentrations in the particulate matter of the estuaries were observed during the rainy season, with $\approx$ 600 mBq g^{-1} in January and March in the Odiel estuary and $\approx$ 1400 mBq g^{-1} in February in the Tinto estuary, probably due to the decrease of pH in the estuaries and consequent coprecipitation/sorption of dissolved U, as discussed below. This behaviour is not observed at the fluvial points, which show more or less constant concentrations during the year, with the highest values (> 100 mBq g^{-1}) during the summer months.

The percentage of ^{238}U associated with the particulate matter at the sampling points weas determined (Table S7 of the supplementary material). In general, the particulate ^{238}U shows low percentages in both rivers, below 2% in most cases, with a median value of around 1%, which indicates that it is mainly transported in the dissolved phase. During the winter months, a notable increase of this percentage is observed, with a maximum of 55% in the Odiel River in February,

probably due to the high rainfall in this month, and therefore an increase in pH to around 5 (Fig. 3A), producing the U precipitation. Unfortunately, the particulate matter in the Tinto River in this month was not determined. In the estuaries, the percentage of ^{238}U associated with the particulate matter is notably higher than the fluvial one, with means of 9 and 25% in the Odiel and Tinto estuaries, respectively. The maximum values for both estuaries were reached in January, and were 49% in the Odiel River and up to 97% in the Tinto River.

The relationship between the pH and the dissolved ^{238}U activity concentration and the distribution coefficients (K_d) is shown in Figure 6, where it can be observed that the concentration of ^{238}U decreases as pH increases in the rivers. The lowest ^{238}U activity concentrations in the dissolved phase (< 30 mBq L^{-1}) were observed in the pH range from 4 to 6, which are reached during the rainy season in both rivers and estuaries as previously mentioned. For pH values higher than 6, which are observed in the estuarine points mainly during the dry season, the dissolved ^{238}U again increases its concentration, reaching values above the concentration in seawater (40 mBq L^{-1}) at pH values above 7 (Fig. 6A). The precipitation and/or adsorption of U by the particulate matter was low at pH values lower than 4 and higher than around 6 ($K_d \approx 10^2 - 10^4$ L kg^{-1}), while for pH values from 4 to 6, the K_d values were one to two orders of magnitude higher (Fig. 6B). The abnormal maximum values of K_d (> 10^5 L kg^{-1}) observed in the Tinto estuary in January and February are probably due to the increase of U in the particulate matter due to the input of this radionuclide from the PG stacks. This behaviour has been observed in previous studies (Hsi and Langmuir, 1985; Serkiz and Johnson, 1994) and is probably due to the coprecipitation of U with Fe-Mn hydroxides (McKee et al., 1987) in the pH range from 4 to 6. On the other hand, the abnormal increase of dissolved U for pH values > 7 is explained by the existence of redissolution processes and the formation of carbonated complexes (Hierro et al., 2013). Therefore, in the Odiel and Tinto estuaries, U shows a non-conservative behaviour.

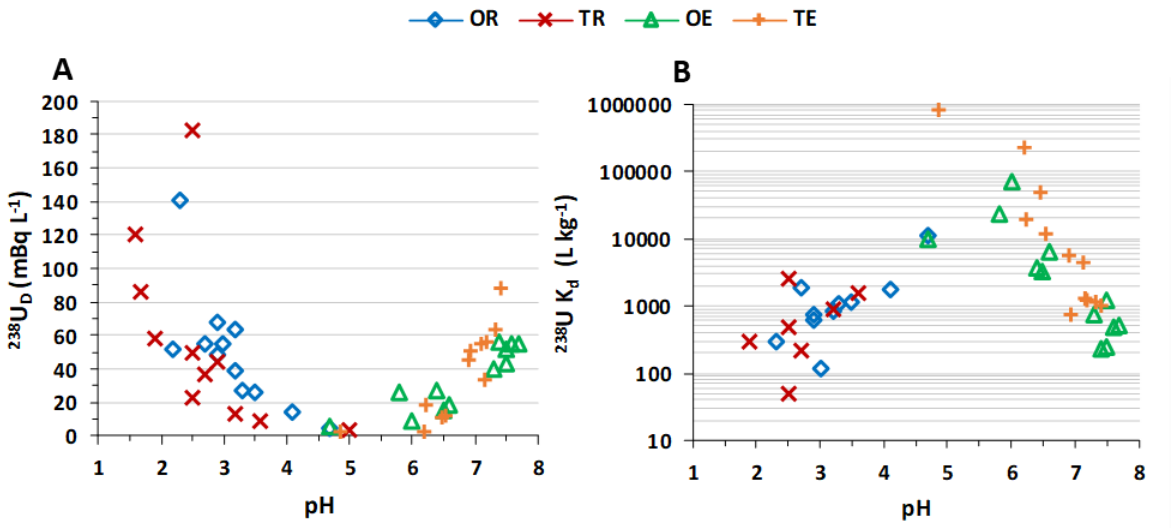

Figure 6. Dissolved ^{238}U activity concentration (A) and ^{238}U distribution coefficients (B) vs pH.

The $^{234}U/^{238}U$ activity ratio (AR_U) in the dissolved and particulate phases was also studied (Fig. 7 and Table S8 of the supplementary material). The AR_U in surface waters is generally higher than secular equilibrium (AR = 1) due to nuclide recoil during alpha-decay of ^{238}U and preferential dissolution of ^{234}U (Henderson et al., 2006). The dissolved AR_U presented values above 1 for most of the samples, with higher disequilibrium in the rivers than the estuaries. Mean values of 1.61 and 1.93 were obtained for the Odiel and Tinto rivers respectively (Fig. 7A), with some values higher than 2 in the Tinto River (Fig. 7B) due to more acidic conditions (Barbero et al., 2014; Manjón et al., 2019a). In the Odiel and Tinto estuaries, the mean values in the dissolved phase were 1.21 and 1.11 respectively (Fig. 7A), very near to the value for seawater (AR_U =1.14) (Boryło and Skwarzec, 2014). AR_U has a similar and constant value in both estuaries during the year, except for January and February (Fig 7B). During these two months, the percentage of fluvial water at the estuarine points is higher than that in seawater, as was previously described, and therefore an increase of the AR_U is expected, as was observed in the Odiel estuary. On the contrary, the Tinto estuary showed values around secular equilibrium, probably due to the great release of polluted leachates from the PG stacks favoured by the rains, which show AR_U around 1 (Gázquez et al., 2014; Pérez-Moreno et al., 2018).

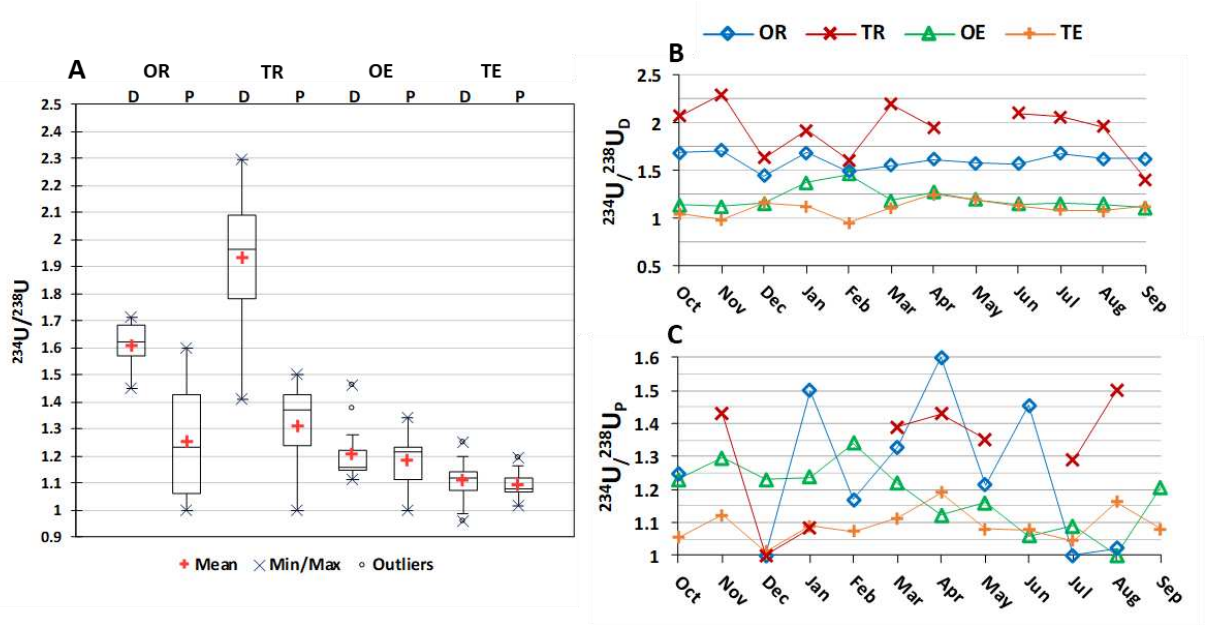

Figure 7. Box whisker plots of the $^{234}U/^{238}U$ activity ratio in the dissolved and particulate phases (A), and temporal evolution for the dissolved (B) and particulate phases (C). Central line: median; box limits: first and third quartiles; whiskers: minimum and maximum non-outliers.

Regarding the particulate matter, lower AR_U values than in the dissolved phase were observed at the fluvial points. The mean values for the Odiel and Tinto rivers were 1.25 and 1.31 respectively (Fig. 7A), ranging from values around the

secular equilibrium up to higher than 1.5 (Fig. 7C). At the estuarine points, the mean values in the particulate phase were 1.18 and 1.09 for the Odiel and Tinto estuaries, respectively (Fig. 7A). The lower observed values of this ratio in the Tinto estuary, mainly during the first half of the studied year (Fig. 7C), are probably once again related to the influence of the PG stacks.

3.3.2 ^{210}Po

The activity concentrations of ^{210}Po in the dissolved and particulate phases are shown in Figure 8 and in Table S9 of the supplementary material. Both rivers and estuaries showed similar dissolved concentrations, with means of around 5 and 0.6 mBq L^{-1} at the fluvial and estuarine points, respectively (Fig. 8A). It highlights the observed dissolved concentration peaks in December in both rivers, with concentrations higher than 20 and 30 mBq L^{-1} in the Tinto and Odiel rivers, respectively (Fig. 8B), one order of magnitude higher than background data observed in surface waters (1–5 mBq L^{-1}; IAEA, 2017). These peaks are probably related to the dissolution of efflorescences precipitated during the dry months (Romero et al., 2006; Sánchez España, 2008; Gázquez et al., 2014) by the first rainfalls of the hydrological year (Fig. S1A, B). In both rivers, the concentrations of dissolved ^{210}Po decrease below 1 mBq L^{-1} during the rainy and increase again to concentrations from 3 to 8 mBq L^{-1} during the summer. In the estuaries, the concentrations of dissolved ^{210}Po are approximately constant during the year around the mean value (Fig. 8B) and are similar to the estimated concentration of this radionuclide in seawater (0.4 to 0.6 mBq L^{-1}) (Skwarzec and Bojanowski, 1988; Uddin et al., 2015) but slightly lower than the concentration on the coast of Huelva (≈ 1 mBq L^{-1}) (Bolívar et al., 2000).

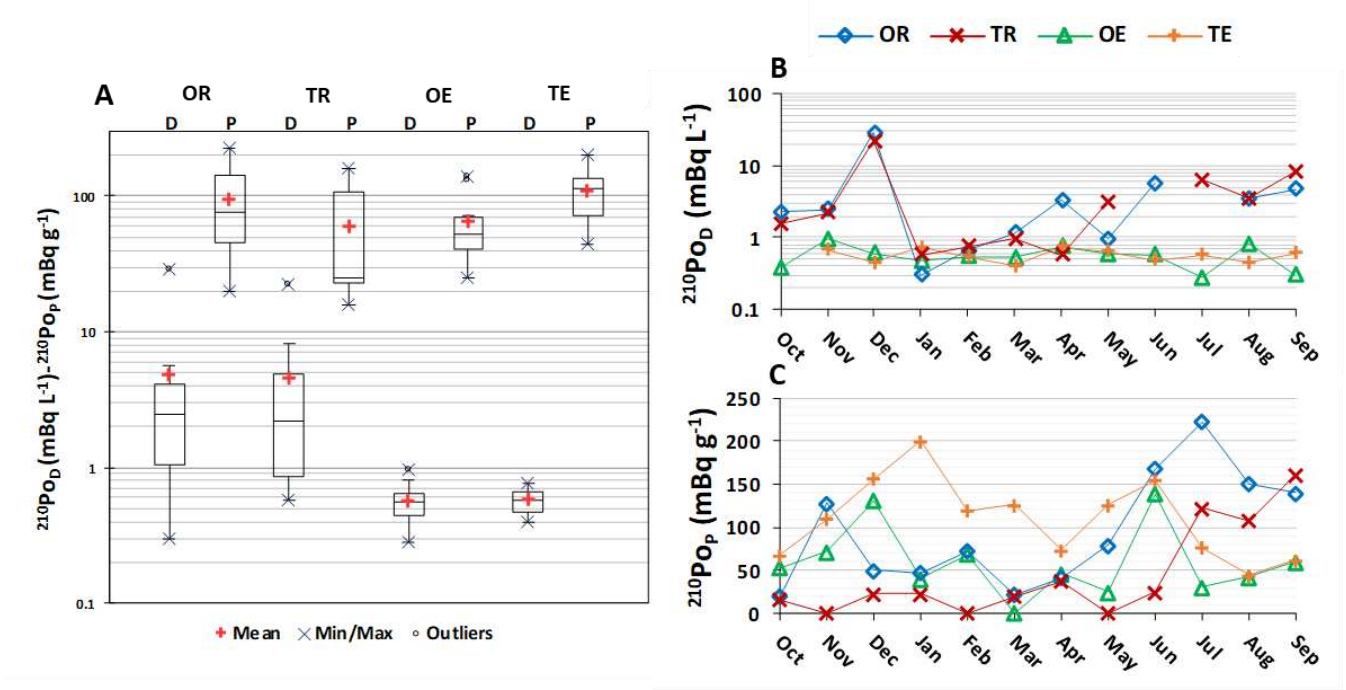

Figure 8. Box whisker plots of the ^{210}Po activity concentration in the dissolved and particulate phases (A), and temporal evolution for the dissolved (B) and particulate phases (C). Central line: median; box limits: first and third quartiles; whiskers: minimum and maximum non-outliers.

In the particulate phase, the concentrations showed mean values of 95 and 59 mBq g^{-1} for the Odiel and Tinto rivers, respectively, and 64 and 110 mBq g^{-1} for the Odiel and Tinto estuaries, respectively (Fig. 8A). These concentrations are two to three times higher than the worldwide median value for natural soils (35 mBq g^{-1}) (UNSCEAR 2000). A great dispersion in the concentrations was observed in both rivers and estuaries during the year (Fig. 8C). While the concentrations are higher in the Odiel River than in the Tinto River, in the estuaries the opposite is observed, with higher concentrations in the Tinto estuary, especially during the rainy season. This fact is probably related to the input from the PG stacks due to the high concentration of this radionuclide in the edge outflows from the piles (mean $\approx 2 \cdot 10^4$ mBq L^{-1}) (Pérez-Moreno et al., 2018). The ^{210}Po shows greater association with the particulate matter than ^{238}U (Table S10 of the supplementary material). The mean values were 25 and 23% in the Odiel and Tinto rivers, respectively, with the highest values during the winter months, as in the case of ^{238}U. A percentage above 60% was obtained in both rivers in January, while during the month of February a percentage above 90% was obtained for the Odiel River. The mean values increased up to 59 and 77% in the Odiel and Tinto estuaries, respectively. These higher percentages of ^{210}Po are indicative of the lower solubility of this radionuclide under estuarine conditions.

^{210}Po tends to decrease its activity concentration in the dissolved phase with an increase in the pH in the studied rivers (pH < 4), similarly to ^{238}U. The dissolved ^{210}Po shows values < 1 mBq L^{-1} in both rivers and estuaries at pH values > 4, and unlike U, does not show an increase in the concentrations at pH values above 6 (Figure 9A). In this sense, Figure 9B shows values of K_d one order of magnitude lower (10^4 - 10^5 L kg^{-1}) at pH below 4 than at higher pH > 4 (> 10^5 L kg^{-1}). These facts demonstrate that ^{210}Po tends to (co)precipitate or to be adsorbed by the particulate matter for pH values higher than 4, showing a non-conservative behaviour. The K_d values are one to two orders of magnitude higher than those of the ^{238}U for the same pH values, which confirms its lower solubility.

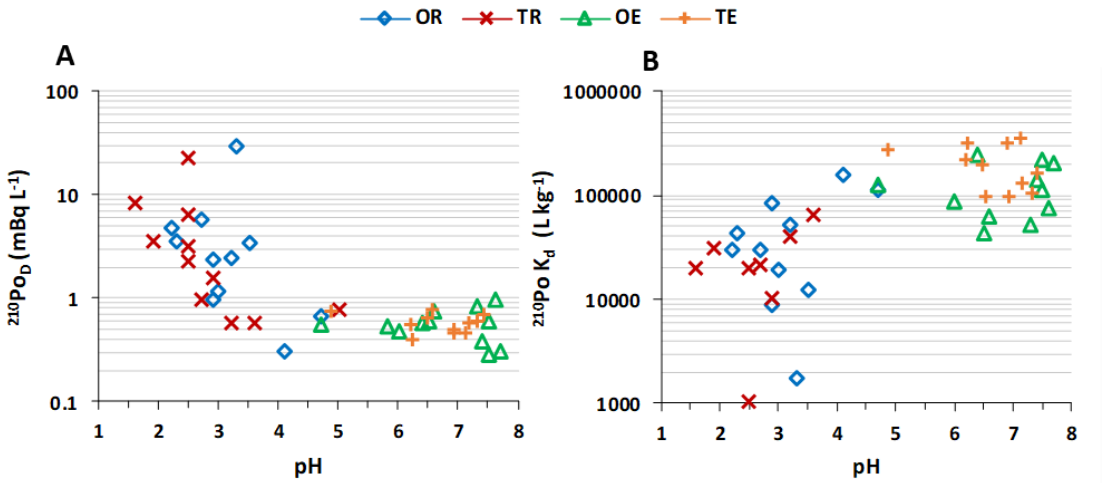

Figure 9. Dissolved ^{210}Po activity concentration (A) and ^{210}Po distribution coefficients (B) vs pH.

3.3.3 Th-isotopes

The results obtained for ^{232,230}Th activity concentration in the rivers are shown in Figure 10. In many cases concentrations below the DL were obtained (Tables S11 and S12 of the supplementary material). Th has a low solubility under neutral conditions, but in waters affected by AMD, due to the high acidity and sulfate concentrations, tends to form soluble sulfate complexes such as $Th(SO_4)^{2+}$ and $Th(SO_4)_{2(aq)}$ (Kim and Osseo-Asare, 2012). Considering only the detected samples, the dissolved phase showed mean concentrations of ^{230}Th and ^{232}Th of 27 and 16 mBq L^{-1} and 53 and 29 mBq L^{-1} in the Odiel and Tinto rivers, respectively (Fig. 10A). The Tinto River generally showed higher dissolved concentrations than the Odiel River, with a maximum of 50 mBq L^{-1} of ^{232}Th and 100 mBq L^{-1} of ^{230}Th, three to four orders of magnitude higher than in surface continental waters (Zhang et al., 2004; Amrane and Oufni 2017; Manjón et al., 2019b). In the estuaries, the dissolved concentrations of these radionuclides were below the DL (≈ 0.5-1 mBq L^{-1}) (Tables S11 and S12), which indicates that Th tends to precipitate due to its high particle reactivity (Wei et al., 2011), showing a non-conservative behaviour in the estuary.

The dissolved concentrations of Th-isotopes also showed a clear seasonal pattern in these rivers, with maxima during the end of autumn and early winter (before the first rains) and during the summer and were below the DL during the rainy season (Fig. 10B). As in the cases of U and Po, this pattern could be explained by three different stages during the year: 1) concentration peaks observed during November and December, probably related to the "washing effect" of salts and efflorescences produced by the first rainfalls after the summer, 2) a "dilution effect" by runoff in the rainy winter, and 3) a progressive "concentration effect" during the spring and summer.

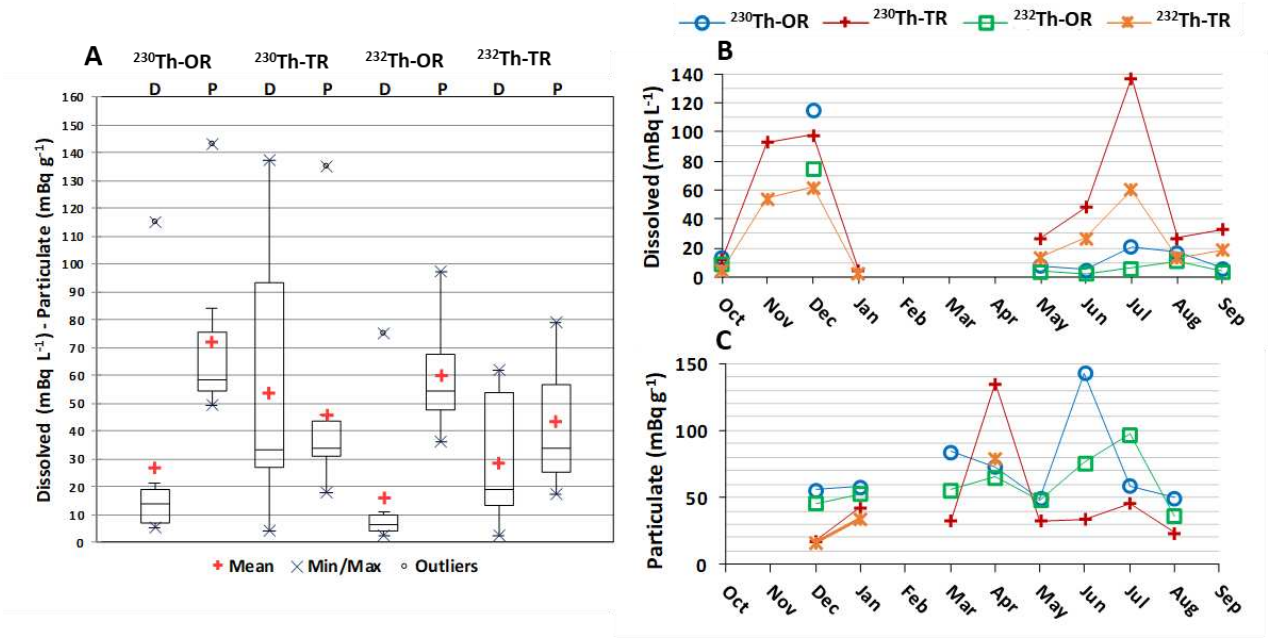

Figure 10. Box whisker plots of the ^{230,232}Th activity concentration in the dissolved (D) and particulate (P) phases (A), and temporal evolution of the dissolved (B) and particulate phases (C). Central line: median; box limits: first and third quartiles; whiskers: minimum and maximum non-outliers.

The particulate matter of the rivers showed mean concentrations of ^{230}Th and ^{232}Th of 70 and 60 mBq g^{-1} and 46 and 43 mBq g^{-1} in the Odiel and Tinto rivers, respectively. At the estuarine points, similar concentrations were observed, with means of ^{230}Th and ^{232}Th of 43 and 17 mBq g^{-1} and 35 and 18 mBq g^{-1} in the Odiel and Tinto estuaries, respectively (Fig. 10A). Despite the abnormally high concentrations of Th-isotopes in the dissolved phase of the rivers, the activity concentrations of ^{232}Th in the particulate phase of the estuarine points are in agreement with the worldwide median concentration in unpolluted soils which is 30 mBq g^{-1} (range: 11-64 mBq g^{-1}) (UNSCEAR, 2000). This could indicate that the precipitation of Th occurs at a point previous to the sampling one. In the rivers, the highest concentrations in the particulate phase were observed during the spring and summer (> 130 mBq g^{-1} of ^{230}Th), with higher values in the Odiel River (Fig. 10C). The estuarine points show a low variability during the year, with slightly higher concentrations during the winter months. For Th-isotopes, the influence of the PG stacks on the Tinto estuary is not observed, probably due to the low concentrations of these radionuclides in the edge outflows (< 100 mBq L^{-1}) (Pérez-Moreno et al., 2018).

4. Conclusions

The evolution and behaviour of U-Th-isotopes and ^{210}Po in two rivers affected by AMD and their common polluted estuary during a year were studied. The conclusions obtained were as follows:

1. The Odiel and Tinto rivers show concentrations of U-Th isotopes and ^{210}Po from one to three orders of magnitude higher than background continental waters due to the impact produced by the AMD. ^{238}U showed a mean concentration

of around 50 mBq L^{-1} in these rivers, with maxima above 100 mBq L^{-1}. ^{210}Po showed a mean concentration around 5 mBq L^{-1} with maxima above 20 mBq L^{-1}. ^{230}Th and ^{232}Th showed maxima above 100 and 50 mBq L^{-1}, respectively.

2. The dissolved AR_U presented high disequilibrium in these AMD polluted rivers, with mean values of 1.6 and 1.9 in the Odiel and Tinto rivers, respectively, and maxima above 2, while in both estuaries a similar mean value to seawater was obtained ($AR_U \approx 1.1$).

3. The studied radionuclides show a clear seasonal behaviour in these rivers, with three different stages during the year: 1) concentration peaks observed during November and December due to the "washing effect" produced by the first rainfalls of the hydrological year, which dissolve the salts and efflorescences precipitated during the dry season, 2) a "dilution effect" by runoff in the rainy winter, and 3) a progressive "concentration effect" during the spring and summer.

4. A non-conservative behaviour of the analysed radionuclides in the estuarine mixing zone was demonstrated due to precipitation processes as a result of the increase of pH. The particulate phase of the estuaries is mainly enriched in U-isotopes and ^{210}Po, with values around one order of magnitude higher than in unpolluted sediments. Maxima of ^{238}U and ^{210}Po above 10^3 and 10^2 mBq g^{-1},respectively, were observed.

5. The polluted outflows from the PG stacks produce a significant radioactive impact on the Tinto estuary, mainly during the rainiest months, increasing the concentration of U-isotopes and ^{210}Po in the particulate matter due to the high concentrations of these radionuclides in the releases and consequent precipitation after the mixing.

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