

1 Determination of trace element concentrations and stable lead, uranium and thorium
2 isotope ratios by quadrupole-ICP-MS in NORM and NORM-polluted sample leachates.

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12 **Abstract**

13 This work focuses on the monitoring of the potential pollution in scenarios that involves
14 NORM related industrial activities (environmental or in-door scenarios). The objective was
15 to develop a method to determine extent and origin of the contamination, suitable for
16 monitoring (i.e. simple, fast and economical) and avoiding the use of too many different
17 instruments. It is presented a radiochemical method that allows the determination of trace
18 element concentrations and $^{206}\text{Pb}/^{207}\text{Pb}/^{208}\text{Pb}$, $^{238}\text{U}/^{234}\text{U}$ and $^{232}\text{Th}/^{230}\text{Th}$ isotope ratios using
19 a single sample aliquot and a single instrument (ICP-QMS). Eichrom UTEVA® extraction
20 chromatography minicolumns were used to separate uranium and thorium in samples
21 leachates. Independent ICP-MS determinations of uranium and thorium isotope ratios were
22 carried out afterwards. Previously a small aliquot of the leachate was used for the
23 determination of trace element concentrations and lead isotope ratios. Several
24 radiochemical arrangements were tested to get maximum performances and simplicity of
25 the method. The performances of the method were studied in terms of chemical yields of
26 uranium and thorium and removal of the potentially interfering elements. The established
27 method, was applied to samples from a chemical industry and sediments collected in a
28 NORM polluted scenario. The results obtained from our method allowed us to infer not
29 only the extent, but also the sources of the contamination in the area.

30
31 **Keywords:**

32 NORM pollution, $^{206}\text{Pb}/^{207}\text{Pb}/^{208}\text{Pb}$, $^{238}\text{U}/^{234}\text{U}$, $^{232}\text{Th}/^{230}\text{Th}$, Quadrupole-ICP-MS,
33 extraction chromatography.

35 **1. Introduction.**

36 Monitoring of industrial-derived inorganic pollution of environmental scenarios has been a
37 constant concern during the last decades, involving the control of toxic element
38 concentration levels. In some specific non-nuclear industries, radioactivity levels must also
39 be controlled, because enhanced levels of naturally occurring radioactive materials
40 (NORM) are handled through various industrial operations [1]. Spread-out problems
41 regarding the NORM industries are the massive use of raw ores containing high
42 concentrations of those radionuclides, forcing thus to monitor not only potentially toxic
43 elements, but also natural radionuclides from ^{238}U and ^{232}Th -Series. The monitoring of
44 those industries is a key matter in the European laboratories due to Chapter 7 from the
45 European Council Directive EURATOM96/29 (1996) [2] and derived subsequent national
46 regulations.

47
48 The monitoring and control of the potential contamination in an area must cover two
49 interrelated aspects: an evaluation of the severity of the potential pollution (by analysing
50 element concentrations) and the origin of the source of pollution, for example using isotope
51 ratios (IRs) such as $^{206}\text{Pb}/^{207}\text{Pb}/^{208}\text{Pb}$ [3-4], $^{238}\text{U}/^{234}\text{U}$ [5-6] and $^{232}\text{Th}/^{230}\text{Th}$ [7-9].

52
53 Two independent instrumentations are commonly required to fulfil both requirements
54 (determination of inorganic pollutant concentrations and isotope ratios). For U and Th
55 isotope ratio analysis a radiometric approach is usually followed (e.g., semiconductor alpha
56 spectrometry). That is combined with the use of AAS, ICP-OES or ICP-MS for the trace
57 element concentrations analyses and MS techniques for lead isotope ratios analysis. The
58 use of a single instrument and a unified method allowing the sequential determination of
59 the inorganic pollutant concentrations and isotope ratios, would simplify laboratory
60 requirements and management.

61
62 Sector focusing ICP-MS instruments offer excellent performance for isotope ratios,
63 although their cost is very high. ICP-QMS measurements can provide all the necessary
64 parameters for a fast monitoring of stable elements and lead, thorium and uranium isotope
65 ratios, minimising the cost of the determinations and saving time. Moreover, the extraction
66 of the required information from the same aliquot minimises sample consumption and also
67 avoids that sample heterogeneities would decouple the results between different kinds of
68 analyses [10] (trace element concentrations and IRs).

69 The low concentration of minor abundance isotopes such as ^{234}U and ^{230}Th , the limited
70 performances of quadrupole instruments for isotope ratio determinations [11-12] and the
71 presence of spectrometric interferences (see below for details) have sometimes precluded
72 the use of ICP-QMS as a routine method for the simultaneous determination of these
73 elements. The application of radiochemical methods previous to the ICP-QMS analysis can
74 resolve some drawbacks of the technique in terms of interferences and limit of detection.
75 There are a large variety of radiochemical methods allowing the separation of U and Th
76 isotopes, many of them designed for measurements by alpha-spectrometry, TIMS or SF-
77 ICP-MS [13-14]. The feasibility of their application to ICP-QMS measurements is not
78 straightforward, since the instrumental limitations, precision, limits of detection and
79 potential interferences vary from those techniques to ICP-QMS. SF-ICP-MS and ICP-
80 QMS instruments use the same technique for analytes' ionization. However, sector field
81 instruments provide signal/background ratios several orders of magnitude larger than
82 quadrupole instruments. Hence, a method designed specifically for SF instruments could
83 use this advantage in order to minimise sample mass amount, i.e. even if the analyte
84 concentration is small in the aspirated solution, the instrumental performances of a SF
85 instrument could overcome this limitation providing enough precision to perform the
86 analysis but it won't be achievable when using ICP-QMS. The methods specifically
87 designed for the analysis by ICP-QMS of isotope ratios of U or (to a minor extension) Th
88 couple subsequent steps of liquid-liquid extraction, ion exchange or chromatographic resin
89 columns or a combination of some of them, hence resulting in time-consuming methods
90 [7,10,15].

91
92 Our aim is to find a suitable radiochemical method that i) concentrates uranium and
93 thorium isotopes with high and reproducible recoveries ii) remove interfering elements to
94 minimise both sample matrix effects and the presence of interferences for ICP-MS
95 measurement iii) allows ICP-MS measurement of uranium and thorium isotopes, together
96 with element concentrations, eventually lead isotope ratios. The implemented method has
97 to fulfil the following criteria a) multi-element analysis and lead, thorium and uranium IR
98 analysis must be performed from a single sample aliquot, b) analyses must be performed
99 exclusively on an ICP-QMS, and c) the method must be as simple (quick) as possible.

100
101 We have tested several methods based on the separation of U and Th using Eichrom
102 UTEVA® resin. Its functional group (diamyl amyolphosphonate, DAAP) has a high affinity

103 for actinides in their tetravalent or hexavalent oxidation state. We focused our work on
104 testing the performances of the selected approaches in terms of feasibility for ICP-QMS
105 measurements. The fractionation of the target analytes (Pb, Th, U and trace elements) and
106 the potential interferences throughout the general scheme has been studied.

107

108 **2. Experimental.**

109 2.1 Sampling scenario

110 Samples were collected in 2001 in the Huelva Estuary (SW of Spain). Contamination in
111 this Estuary (which is formed in the confluence of Odiel and Tinto rivers) has been
112 monitored though the years since it is one of the most contaminated estuaries in the world.
113 It is strongly affected by acid mine drainage (AMD) and phosphoric acid production
114 plants, resulting in high concentrations of heavy metals such as Fe, Cu, Zn and Mn [15-
115 16].

116

117 Furthermore, several phosphoric acid production plants discharged wastes to the Odiel rier
118 through years. The main used ore was phosphate rock (PR) from Morocco containing high
119 activity concentrations of U-Series radionuclides under nearly secular equilibrium [5]. The
120 discharged waste, phosphogypsum (PG), contains large fractions of radium, thorium and
121 lead isotopes.

122

123 2.2 Samples and reagents.

124 The analysed samples comprise NORM matrices (PR and PG) and NORM-polluted
125 riverbed sediment samples. The samples were stored in polyethylene sealed bottles. Before
126 analysis, the samples were dried at 65°C to a constant weight and sieved by 10 µm mesh.

127

128 Suprapure grade HNO₃, H₂O₂ and HCl (Merck) and 18.0 MΩ cm⁻¹ deionised water
129 (Millipore) were used for samples leaching, chromatographic separations and solution
130 matrix adaptation, when required. Al(NO₃)₃ and oxalic acid (Panreac) were analytical
131 grade. 2 mL pre-packed minicolumns of Eichrom's UTEVA resin (TRISKEM, France)
132 were used for the chromatographic separation and purification of Th and U.

133

134 2.3 ICP-MS setup.

135 Quantitative elemental analysis and isotope ratio determinations were carried out using an
136 Agilent 7500c ICP-QMS provided with an Octopole Reaction System (ORS). Operating

137 conditions are provided in Table 1. Element concentrations (Pb, Th, U and interfering
138 elements), quality checks, recoveries/interfering elements decontamination monitoring and
139 the calculation of dead time for count rates correction were carried out using a mix of
140 single element standard solutions diluted to the required concentrations. The U.S. E.P.A.
141 200.8 methodology was used in order to check for calibration accurateness and precision
142 and to test the presence of memory effects, sample matrix effects, etc.

143
144 Isotope ratio analyses were done using a PFA-100 micronebuliser working under self-
145 aspiration regime being the ORS off. Mass bias correction was performed by bracketing
146 the samples between certified IR standard solutions and a blank solution using the linear
147 approach. NIST-981, NIST, U.S.A. was used for lead. IRMM-035 and IRMM-056 were
148 used for thorium and uranium, respectively (Institute for Reference Materials and
149 Measurements, Geel, Belgium). Every four samples, a certified reference material solution
150 or a replicated sample was analysed as an unknown sample in order to test the accuracy,
151 short-term analysis reproducibility and precision of the results.

152
153 Standard solutions of lead, thorium and uranium at the 10 ng mL^{-1} concentration level were
154 self-aspirated using different dwell times in order to minimise the internal uncertainty.
155 Dwell time was fixed for every isotope to be considered in the isotope ratio calculations,
156 and the relative standard deviation (RSD) dependence with element concentration was
157 studied as suggested in previous works [18-19]. Therefore, it is possible to establish a
158 concentration discrimination level providing enough counting statistics to produce the
159 required RSD level. In our case, it has been established at the 3% level, which is a typical
160 value of relative counting uncertainty in alpha spectrometry. Data from Figures 1.a and 1.b
161 show that these values are obtained when activity concentrations in the aspirated solutions
162 range 0.25 mBq mL^{-1} for ^{234}U and 0.7 mBq mL^{-1} for ^{230}Th .

164 2.4. Radiochemical procedure.

165
166 Element concentrations and lead isotope ratios were determined after applying the
167 U.S.E.P.A. 3050B method, filtrating and subsequently diluting a small aliquot of the
168 filtrate. This method does not provide total sample dissolution but it offers a reasonable
169 assessment of the worst-case environmental scenarios where components of the sample
170 become soluble and mobile [20]. Total digestion of the sample requires either alkaline

171 fusion (which introduces extremely high sample matrix effects requiring dilution factors
172 that could make difficult analytes quantification, [21]) or the use of hydrofluoridric acid
173 (see, e.g., [22]), which is highly toxic, cannot be introduced into our ICP-QMS instrument
174 and must be previously removed by evaporating or by reaction with boric acid. However,
175 boric acid produces intense matrix effects unless very large dilution factors are applied
176 [23], and evaporation can lead to uncontrolled analyte losses in volatile compounds. Since
177 the aim of this work is to develop a fast method for NORM contamination monitoring, the
178 digestion of the refractory matrix is not indispensable. Previous works supports this
179 approach. They establish that to infer the source of the pollution in NORM samples the
180 information required (elements and isotope ratios) can be achieved without performing
181 total sample dissolution [24-28]. On the other hand, it will improve the robustness of the
182 chemical separation, since the incorporation of methods to dissolve the refractory matrix
183 can seriously affect the performances of the chromatography columns [22]. After leaching
184 and filtration, a small aliquot is diluted for element concentration and lead isotope ratios
185 analyses, while the remaining solution is used to concentrate and purify uranium and
186 thorium.

187
188 The extraction efficiency of the leaching method was tested through analysis of certified
189 reference samples IAEA SL-1 and NIST SRM-1646 (lake and estuarine sediment samples
190 respectively). It was better than 75% for Mg, V, Cr, Mn, Fe, Co, Zn, As, Cu, Pb and U; it
191 was comprised between 50 and 75% for Th, and it was less than 50% for Al, Ca and Ti.
192 Short-term repeatability (~ 3 days) of the leaching efficiency was better than 10% through
193 4 sample replicates, excepting for Al, Ca and Ti [29]. Regarding stable lead isotope ratios,
194 the analyses of the IAEA SL-1 sediment reference samples provided results for $^{206}\text{Pb}/^{207}\text{Pb}$
195 isotope ratio (1.219 ± 0.003) in good agreement with those provided by Lindeberg et al.
196 (1.217 ± 0.003) [30].

197
198 The radiochemical setup was based on the one by Horwitz et al. [31], designed to be
199 coupled with alpha-spectrometry. Several modifications were made to the original method,
200 in order to improve its performances; the six different options tested, which are based in
201 references [31-35] are displayed in Figure 2, and they were applied in order to avoid
202 stripping together U and Th [36] due to the potential overlapping of thorium hydrides on
203 uranium isotopes. Every radiochemical procedure was tested using 2-4 sample replicates.
204 All the tests were performed using true sediment samples instead spiked artificial

205 solutions. The fractionation of potential spectrometric interferences throughout the applied
206 procedures was also analysed. All the solutions generated during each radiochemical
207 scheme (leaching solution, loading elute, wash elute, conditioning elute, thorium stripping
208 solution and uranium stripping solution) were submitted to multielemental analysis after
209 convenient dilution.

210

211 The main interferences potentially overlapping the masses of our interest (Pb: 206, 207,
212 208; Th: 230, 232; U: 234, 238) are Tl hydrides (lead isotopes), Cd and In dimers and Os
213 and Pt argides (at mass 230), Sn dimers and Os argides (232), Sn dimers, Pt and Hg argides
214 and Th hydrides (234) and Sn dimers and Pt argides (238). A feasible method fitting to the
215 criteria previously established must allow separation of U and Th isotopes, and a
216 convenient removal of Cd, In, Os, Pt, Hg and Sn.

217

218 A comparison among the concentrations found in the leachate and those other
219 concentrations found in those solutions allow us to calculate the chemical yield of each
220 element (both analyte and interferences) in each solution, avoiding in this way the use of
221 chemical yield tracers for U and Th and allowing the evaluation of the impact of
222 interferences in U and Th less abundant isotopes. All the uncertainties have been given
223 account by expansion according to GUM guide, excepting type-B uncertainties, which
224 could be important when considering the samples' dilution factors.

225

226 **3. Results.**

227

228 The recoveries of U and Th were tested for different setups using the options described
229 above (Table 2). According to their chemical yields and crossover, **the most suitable setups**
230 **(E and F)** were selected. The differences of fractionation behaviour for U and Th
231 depending on the nature of the sample were tested using sediment and PG samples (Figures
232 3.a and 3.b). Their performances were also analysed in terms of trace element fractionation
233 (Table 3) and capacity of decontamination of interfering elements (Table 4). For the
234 reasons explained below, the procedure E was chosen. It was validated for U, Th and IRs
235 using sediment, phosphogypsum and phosphate rock samples previously submitted to
236 intercomparison exercises or previously analysed by using conventional, well-established,
237 radiometric methods in our research group (Table 5). The potential of the method to detect
238 not only the levels of contamination, but also to deduce the source of the contamination,

239 was tested measuring environmental samples from the Huelva estuary. Results are
240 provided in Tables 6 (trace element concentrations) and 7 (U and Th activity
241 concentrations and IRs) and Figure 4 (Pb IRs).

242

243 **4. Discussion.**

244 4.1. Chemical fractionation of Th and U.

245

246 Setup A produced high recoveries for uranium but very low recoveries for thorium (Table
247 2), unlike other authors [32,35] that obtained good recoveries for thorium using setup A in
248 coral (mainly calcium carbonate), uranite and MOX samples analyses. It was found that Th
249 remained unstripped within the resin. The success of this method for Th measurement
250 depends on the sample matrix. In this case the main components of our matrices, silicates
251 and phosphates, might prevent the solubilisation of Th [37]. No significant differences
252 among setups A and B were detected: hydroxides precipitation did not introduce any
253 difference in the performances of the resin. The results suggest that both setups are to be
254 discarded. No higher HCl concentrations were tested as according to Kd published values
255 [31], that could increase U recovery, but not Th recovery.

256

257 The application of setups C and D produced higher recoveries in Th than setups A and B
258 but U recoveries decrease slightly. Thorium and uranium were not fully extracted from the
259 column; furthermore, the application of this Th stripping procedure leads to a high
260 crosstalk. U is extracted using low HCl concentration, where Kd-values of Th for UTEVA
261 resins are low. Therefore, a certain amount of Th might remains unstripped within the resin
262 bed, being eluted during the uranium stripping. The higher the Th fraction retained in the
263 resin, the higher the fraction leaking into the U fraction. The retained fraction is higher
264 when Th linkage to the resin during the sample load is weaker (i.e., using 3M HNO₃, setup
265 C, instead 1M Al(NO₃)₃/3M HNO₃, setup D). No higher HCl molarities were tested as that
266 could increase the uranium recoveries, but not thorium recoveries.

267

268 The method that best performs is setup E. Cross contamination is negligible and recoveries
269 of both U and Th are high enough as to provide adequate concentrations for the
270 determination of isotope ratios. However, this setup includes an actinide precipitation step,
271 which increases sample preparation time in approximately 5-10%. In order to check if this

272 step can be skipped, setup F was tested, avoiding the hydroxide precipitation step. In this
273 case, the recoveries of Th were less than for setup E.

274

275 Regarding the differences found for different sample matrices (Figures 3.1 and 3.2),
276 uranium recoveries were high for both matrices. Recoveries were some 10% higher when
277 no precipitation was applied to sediment samples (no uranium was detected in the
278 supernatant phase). The slightly decrease for phosphogypsum samples is probably due to
279 the high phosphates concentration in PG matrices. Phosphates act as complexing agents of
280 uranium nitrate, preventing its adsorption to DP[PP] extractant matrix in the UTEVA resin
281 on spite the $\text{Al}(\text{NO}_3)_3$ added. This would explain the detection of uranium in both load and
282 conditioning solutions.

283

284 The results for setups E and F show important differences for thorium. With no hydroxide
285 precipitation in sediment samples, Th extraction recovery was greatly reduced, and
286 crossover in the uranium fraction was observed. The results showed that during the
287 application of setup F, thorium was weakly adsorbed to resin. That process leads to
288 **important** losses of thorium during the steps of sample loading, resin washing and others
289 when PG was processed. Therefore procedure F cannot be fully recommended.

290

291 4.2. Chemical fractionation of trace elements.

292

293 As shown in Table 3, most of all the elements show the same behaviour regardless their
294 geochemistry (lithophile, siderophile, chalcophile), the applied setup (E or F) or the matrix
295 sample. Pb follows loading solution, hence in this case adapting the sample before isotopic
296 analysis is very simple. The largest fraction of the other elements is lost during the solution
297 loading into the column and the subsequent washing of the resin. However, several
298 exceptions might appear.

299

300 A higher fraction of Ca, Sr, Co, Ni, Cu, Zn and Tl remains in the supernatant fraction when
301 the actinide precipitation is applied. The removal of Ca is especially important for the
302 determination of Th and U isotopes by ICP-QMS since a very high Ca concentration in the
303 aspirated solution leads to a drastic decrease of instrumental response to actinides [36]. It
304 might be especially important for PG samples, since Ca is approximately 20% of the total

1 305 sample mass. Thus the application of a previous precipitation step is recommended as a
2 306 way to better purify U and Th fractions.

3 307

4 308 If a high Tl concentration were present in a sample, Tl hydrides could interfere in ^{206}Pb
5 309 count rates in the first leaching filtrate. When Tl concentration (either naturally present in
6 310 the sample or spiked) is similar to Pb concentration, it could be alternatively used for
7 311 internal mass bias correction. Therefore, this element fractionation should be kept in mind,
8 312 and it is found again that the application of the hydroxides precipitation is a good method
9 313 of sample purification. In case that high Tl concentration were found in the leaching
10 314 filtrate, lead isotope ratios could alternatively be measured in the precipitate, once a large
11 315 proportion of Tl is removed.

12 316

13 317 Small fractions of Ti, Cr and Zn were detected in U and Th eluates. Besides, small
14 318 fractions of Tl, Mn, Fe, Cu and Pb can also be sometimes detected in uranium eluates.
15 319 Such fractions do not cause counting interferences in U and/or Th measurements.
16 320 Furthermore, they were detected mainly in the eluates produced after application of setup F
17 321 to PG samples but not if the iron hydroxide precipitation is applied (Method E).

18 322

19 323 Interfering elements Os, Au and Hg were not detected in any of the analysed phases. This
20 324 is due to the combination of a small concentration in the sediment sample and the
21 325 application of a high dilution factor for ICP-QMS measurement. By monitoring the U/Th
22 326 fractions, it was found that their counting rates were below those achieved for ^{234}U and
23 327 ^{230}Th isotopes by even more than one order of magnitude. As a result, the expected count
24 328 rate contribution of Os, Au and Hg derived argides to total count rates on masses 230 and
25 329 234 were negligible.

26 330

27 331 Cd, In, Sn and Pt (Table 4) were detected in some of the elutions from the radiochemical
28 332 setup. On the contrary to Os, Hg and Au, the complete mass balance can be established for
29 333 the three first elements (not for Pt due to very low concentrations), as the analysed
30 334 solutions contained 90-100% of masses introduced during the leaching. The removal of a
31 335 large fraction of Cd can be achieved through the previous precipitation step with iron
32 336 hydroxide (setup E). On the contrary, In and Sn remain mainly in the precipitate. However,
33 337 a large fraction of these elements followed the loading and the washing solution and were
34 338 not retained by the resin.

339

340 Indium small mass rates remained in the Th fractions when no actinide precipitation was
341 applied. The In initial concentration present in the sample was already small, hence the
342 expected counting rate associated to ^{230}Th is several orders of magnitude higher than those
343 due to In and no important interferences are expected. Relatively large fractions (~20%)
344 remain in the uranium phase, however In dimers do not overlap uranium isotopes.

345

346 Finally, the fraction of Sn lost during the loading into the column is significantly higher
347 when the precipitation is applied. A small but measurable amount remains in the uranium
348 fraction when no precipitation is applied.

349

350 It can be concluded that the procedure E allows Pb isotopic analysis after a convenient Tl
351 removal (if required), being dilution factors near 2000 mL/g for Pb and approximately
352 20000 mL/g for Tl in case lead is analysed in loading solution instead of the diluted
353 leachate. In both cases RSD values in the range of 0.3 % were achieved in the
354 corresponding isotope ratios.

355

356 Setup E was therefore chosen as the most suitable method and was used for the rest of this
357 work. For a set of 5-10 samples, the application of this method consumes in the range of 2-
358 2.5 working days at the laboratory, and additionally some 20 minutes per sample are
359 required for isotope ratio analysis, which is thus convenient when compared to the
360 approximately 2-3 days of counting time required for alpha particle spectrometry.

361

362 4.3. Validation of the technique.

363 Table 5 shows the results obtained for several PR, PG and sediment samples used for
364 validation as described in section 3. Concentrations obtained using setup E + ICP-MS were
365 in agreement within the uncertainties to the results obtained by alpha spectrometry. Isotope
366 ratios were in good agreement within a 1- σ confidence interval after calculation of A-type
367 expanded uncertainties according to GUM approach.

368

369 Uncertainties for uranium and thorium isotope ratios are within the ranges 0.6-2.5% and
370 2.3-5 % respectively. They are comparable to or slightly better than those obtained by
371 alpha spectrometry, which are within a range 1.6-3 % for uranium isotope ratios and within

372 a range 4-8 % for thorium isotope ratios. These results show the potential for the
373 application of this methodology to NORM samples.

374

375 Regarding major isotope activity concentrations, those obtained by ICP-MS are less than
376 or equal to those obtained by alpha spectrometry, as expected, bearing in mind that no
377 chemical yield tracer were applied during the radiochemical separation.

378

379

380 4.4. Application to environmental samples

381

382 The results for Cr, Mn, Ni, Cu, Zn, As, Cd and Pb (Table 6) are in good agreement with
383 previously published values for this area [16, 38]. These results reflect the effect of the
384 mining activity on the estuarine sediments, being the concentration levels of some
385 elements (Cu, Zn, As, Pb) systematically higher than “Effects Range-Median” (ERM)
386 levels of sediment quality guidelines provided in [39]. Cd and Ni levels are also above
387 ERM values in several samples, and systematically higher than “Effect-Range-Low”
388 (ERL) values.

389

390 PG and PR samples are not affected by acid mine drainage (AMD). Almost all the
391 concentrations of elements in PR were below the concentrations found in unpolluted
392 sediments, excepting for the radioisotopes from ²³⁸U-Series and Cd. Trace element
393 concentrations in PG are below natural background values in the area, being the only
394 exceptions Ca (matrix element in the PG) and Sr due to its geochemical similarity to Ca.
395 Mn concentrations in PG, which are several orders of magnitude below the values in PR,
396 suggest that Mn is probably associated to the P₂O₅ fraction during the industrial process.

397

398 The results of Table 7 for uranium isotope ratios are in good agreement with those found in
399 [6,26]. These values are for sediment samples statistically significantly less than 1.0. The
400 values here found for ²³²Th/²³⁰Th isotope ratios are below those found by Bolivar et al. [6]
401 by a factor ~2. Isotope ratios in the range of ~ 0.7±0.2 could be considered as almost
402 representative values of unpolluted sediments in this area [8]. The other samples showed
403 thorium isotope ratios that range 0.06-0.13, whereas the values in PG range 0.012-0.018.
404 Those samples having low Th IR values are reflecting the mixing of the isotopic signals

405 due to natural processes and that other associated to industrial activities (see below for
406 details).

407

408 The low concentration and the large dilution factor used did not allow the determination of
409 the Pb isotope ratios in phosphogypsum samples. For sediment samples, a good
410 correlation among $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ was found ($r = 0.9762$, significance better
411 than 0.01%). It is worth to mention a few important facts: the values are scattered around
412 the characteristic fingerprint values published for the Iberian Pyrite Belt IPB [40], which
413 pyrite and galena ore deposits are expected to be the main contributors to the lead
414 accumulated in the sediments. The significant deviations from the IPB characteristic values
415 indicates the mixing with additional sources such as emissions from road traffic and coal
416 burning in the surrounding industry [3].

417

418 The final aim of the methodology proposed is to evaluate the degree and origin of
419 contamination in samples. The possibility of using our multiple IR data for categorization
420 of data has been explored by a cluster analysis using the sediment samples results.
421 $^{208}\text{Pb}/^{207}\text{Pb}$ IR has been not included due to its linear dependence with $^{208}\text{Pb}/^{207}\text{Pb}$ IR.
422 Figure 5 shows the dendrogram allowing the identification of three large groups of samples
423 according to their respective IRs: 1) high Th IRs (0.184-0.397), high $^{206}\text{Pb}/^{207}\text{Pb}$ ratios
424 (1.1662-1.1760) and low U IRs (0.871-0.894), 2) intermediate Th IRs (0.0829-0.204),
425 $^{206}\text{Pb}/^{207}\text{Pb}$ close to IPB signature and high U IRs (0.934-0.959), 3) low to intermediate Th
426 IRs (0.06-0.13), low $^{206}\text{Pb}/^{207}\text{Pb}$ IRs (1.1504-1.1552) and intermediate U IRs (0.919-
427 0.941). The third group associates to mixing of sediments suffering a large entrance from
428 road pollution and liquid discharges from fertilizers plants. The second group corresponds
429 to samples showing a large AMD signal mixed with settling sediment from Odiel river
430 previously affected by fertilizers factories. The first group of samples comprises samples
431 having less intense pollution from fertilizers factories and great impact of additional
432 sources of lead: the effect of runoffs from soil cannot be discarded. The distinctive signals
433 that we are able to detect and identify, combining IR measurements and a cluster analysis,
434 highlight the good performances of our technique to evaluate contamination patterns.

435

436 5. Summary and Conclusions.

437

438 Different methods have been tested and tuned for the characterization of trace element
439 concentrations and lead, uranium and thorium isotope ratios from a same sample aliquot
440 using ICP-QMS. According to the results found for U and Th recoveries, cross
441 contamination and the presence of potential spectrometric interferences, setup E was
442 chosen. This procedure allows recoveries for U and Th nearly 90% and 75%, respectively
443 being their respective fractions of purity enough as to provide accurate and precise results.
444 The application of this methodology to environmental samples from a quite polluted
445 scenario shows the potential to collect information on the extension and the origin of
446 pollution on a routine basis and using an only conventional instrument (ICP-QMS). This
447 fact leads to simplify laboratory requirements and management.

448

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450

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456 and facilities of the Radioisotopes Service.

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458 **7. References.**

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626 FIGURE CAPTIONS.

627
628 Figure 1.1: Dependence of $^{238}\text{U}/^{234}\text{U}$ isotope ratio value (expressed in terms of activity
629 ratio) and RSD with ^{234}U concentration.

630
631 Figure 1.2: Dependence of $^{232}\text{Th}/^{230}\text{Th}$ isotope ratio value (expressed in terms of activity
632 ratio) and RSD with ^{230}Th concentration.

633
634 Figure 2: Radiochemical combinations used in this work.

635
636 Figure 3.1: U fractionation through the procedures described in the text as setups E and F.

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637 Sup: Supernatant. T: Th fraction. U: U fraction. Wash and Cond are the column eluates
638 after washing the resin and conditioning it to the chloride form, respectively.

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640 Figure 3.2: Th fractionation through the procedures described in the text as setups E and F.
641 Sup: Supernatant. T: Th fraction. U: U fraction. Wash and Cond are the column eluates
642 after washing the resin and conditioning it to the chloride form, respectively.

643
644 Figure 4: Stable lead isotope ratios found in the sediment sample leachates analysed in this
645 work. Shaded zone marks the signature values corresponding to galena and pyrite samples
646 from the Iberian Pyrite Belt according to Pomiés et al. (1998).

647
648 Figure 5: Dendogram obtained after cluster analysis of the isotope ratios collected for the
649 sediment samples described in the text.

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RF Power (W)	1550, torch shield
Sampling depth (mm)	5.9
Quantitative analysis mode	
Carrier gas (L min ⁻¹ , Babington nebuliser)	1.1
ORS	H ₂ (4.5 L min ⁻¹), He (2.5 L min ⁻¹)
Internal standard	⁶ Li, ¹⁰³ Rh, ²⁰⁹ Bi
Sample flow rate (L min ⁻¹)	0.4
Replicates	3
Isotope ratio mode	
Carrier gas (L min ⁻¹ , PFA nebuliser)	0.5
Auxiliary gas (L min ⁻¹)	0.4
ORS	Off
Sample flow rate (L min ⁻¹)	0.05
Dwell time (ms)	230: 30, 232: 1; 234: 25; 238: 0.9
Replicates	7-10
Ce ¹⁶ O ⁺ /Ce ⁺ (%)	0.7-1.2
Th ¹ H ⁺ /Th ⁺ (%)	(1.0-1.4)·10 ⁻³
(M-1) ⁺ /M ⁺ (%)	<4·10 ⁻²
(SnSn) ⁺ /Sn ⁺ (%)	<4·10 ⁻⁴
Mass bias correction	External, linear

Table 1. Operating conditions of the Agilent 7500c ICP-QMS used in this work.

Phase / Setup	A (n=3)	B (n = 3)	C (n=2)	D (n=2)	E (n= 4)	F (n=4)	F* (n=4)
U in phase U (%)	98.2±0.4	94.6±0.9	74.2±0.8	76±2	89±2	102±3	70.1±1.0
U in phase T (%)	3.7±0.3	2.7±0.4	2.77±0.03	1.45±0.03	N.D.	N.D.	N.D.
Th in phase U (%)	N.D.	N.D.	26.2±0.3	42.0±0.5	N.D.	3.0 ±0.5	1.82 ±0.03
Th in phase T (%)	6.59±0.15	2.3±0.6	44.4±0.9	23.7±0.4	74±2	41±3	56.1±0.7

Table 2. Results (mass rates) obtained for U and Th in the fractions corresponding to uranium and thorium after application of setups A-F. Mass rates were calculated as described in the text. All the tests were applied to sediment samples except F*, which is the setup F applied to PG samples. Setup A combines the options I+a+1 shown in Figure 2. Setup B: II+b+1, Setup C: II+a+2, Setup D: II+b+2; Setup E: II+b+3. Setup F: I+b+3. Phase U and T are stripping solutions for uranium and thorium, respectively. N.D: not detected.”

	Sup.	Load	Washing	Cond.	Th	U
Sediment (setup E)						
Mg	9.2 ± 0.9	85 ± 3	10.7 ± 0.4	0.39 ± 0.04	N.D.	N.D.
Ca	49.8±1.8	37.1±1.1	11.6±0.2	N.D	N.D	N.D.
V	0.31±0.04	96 ± 3	12.3 ± 0.4	0.61 ± 0.03	N.D.	0.013 ± 0.005
Cr	0.25±0.04	99 ± 3	12.5 ± 0.4	0.63 ± 0.04	N.D.	N.D.
Mn	0.87±0.06	74.5±1.9	9.52 ± 0.25	0.425±0.014	N.D.	N.D.
Co	40.1 ± 1.3	30.7±1.0	4.07 ± 0.12	0.307±0.009	N.D.	N.D.
Ni	98 ± 10	7.8±0.9	0.3 ± 0.3	0 ± 3	N.D.	N.D.
Cu	86± 3	12.3±0.4	1.65 ± 0.05	0.105±0.004	N.D.	N.D.
Zn	52.8 ± 2.1	8.9±0.3	0.86 ± 0.04	N.D.	N.D.	N.D.
As	0.78±0.19	80.1±2.3	10.1 ± 0.3	0.52 ± 0.04	N.D.	N.D.
Sr	53.5 ± 1.5	26.2±0.7	3.51 ± 0.09	(48±21)·10 ⁻³	N.D.	N.D.
Mo	48 ± 4	50±3	8.4 ± 0.6	2.92 ± 0.16	N.D.	N.D.
Tl	70.1±2.4	4.6±0.6	12.1±0.7	3.6±0.7	4.3±0.2	3.6±0.3
Pb	0.36±0.05	87.4±1.8	11.67±0.24	0.517±0.011	N.D.	N.D.
Sediment (setup F)						
Mg	-	95± 23	12±12	N.D.	N.D.	N.D.
Ca	-	82.6±2.2	20.1±5.5	N.D.	N.D.	N.D.
V	-	102.2±1.4	15.32±0.12	N.D.	N.D.	N.D.
Cr	-	102.9±1.0	15.44±0.15	1.8 ± 0.05	0.417 ± 0.013	0.264 ± 0.011
Mn	-	95.3±1.3	15.95±0.12	N.D.	N.D.	0.05 ± 0.03
Co	-	100.2±1.4	15.44±0.15	N.D.	N.D.	N.D.
Ni	-	103.3±1.7	13.0±0.17	N.D.	0.539 ± 0.022	0.209 ± 0.014
Cu	-	81.9±1.4	13.44±0.11	N.D.	5.5 ± 0.3	5.7 ± 0.9
Zn	-	77.1±2.1	15±8	N.D.	N.D.	N.D.
As	-	102.4±1.5	15.75±0.04	0.39±0.08	N.D.	N.D.
Sr	-	68.2±1.5	32±4	N.D.	N.D.	N.D.
Mo	-	N.D.	N.D.	N.D.	9.22 ± 0.15	8.92 ± 0.12
Pb	-	105.4±2.1	N.D.	N.D.	0.174 ± 0.004	N.D.
Tl		72.3±2.2	16.6±2.1	3.3±0.6	5.33±0.2	5.1±0.3
Phosphogypsum (setup F)						
Mg	-	29.7±1.7	0.047±0.013	N.D.	N.D.	0.48 ± 0.08
V	-	72.7±1. 1	7.47 ± 0.18	7.1 ± 0.7	1.78 ± 0.20	0.869 ± 0.019
Cr	-	79.5±1.7	5.20±0.22	2.9 ± 0.3	N.D.	1.03 ± 0.06
Mn	-	59 ± 4	N.D.	14.3 ± 4.7	N.D.	9.N.D..8
Co	-	89 ± 4	N.D.	8.94 ± 0.13	N.D.	1.033 ± 0.013
Ni	-	41.2±0.7	0.59±0.22	N.D.	N.D.	N.D.
Cu	-	94 ± 4	N.D.	9.9 ± 0.7	14.0±0.8	6.86 ± 0.19
Zn	-	72 ± 3	3.41±0.12	N.D.	2.40±0.12	1.42 ± 0.11
As	-	90 ± 5	N.D.	6 ± 4	N.D.	N.D.
Sr	-	48.2±0.5	3.73±0.04	0.21±0.09	0.043 ± 0.011	N.D.
Mo	-	0±5	21.2±1.1	19 ± 4	4.2 ± 1.0	30.3 ± 1.5
Tl	-	73.6±3.8	13.6±2.3	8.3±0.8	3.32±0.23	1.1±0.4
Pb	-	99.8±1.2	14.01±0.23	6. 3 ± 0.6	N.D.	3.84 ± 0.10

Table 3. Summary of elements fractionation (%) for sediment and phosphogypsum samples. 3 replicates were performed per test. The results are shown as weighted averages \pm weighted uncertainty. Sup: Supernatant (after hydroxide precipitation, if any). Load: Elute obtained after loading U and Th in the resin. Wash and Cond. are the solutions collected after washing the resin and conditioning it to chloride form.

N.D: Not detected.

Phase	Supernatant	Load	Conditioning	Wash	Thorium	Uranium
			Sediment (Setup E)			
Cd	66 \pm 2	13.9 \pm 0.7	2.44 \pm 0.12	N.D.	N.D.	N.D.
In	0.22 \pm 0.05	84 \pm 2	11.1 \pm 0.4	0.41 \pm 0.10	N.D.	N.D.
Sn	3.2 \pm 0.3	85 \pm 4	11.3 \pm 0.5	N.D.	N.D.	N.D.
Pt	0 \pm 0	20 \pm 48	3 \pm 6	N.D.	4 \pm 2	7 \pm 5
			Sediment (Setup F)			
Cd		88 \pm 1	N.D.	N.D.	N.D.	N.D.
In		73 \pm 7	12 \pm 3	N.D.	1.4 \pm 0.3	21 \pm 2.3
Sn		52.0 \pm 1.5	3.82 \pm 0.16	N.D.	1.27 \pm 0.06	2.2 \pm 0.6
Pt		N.D.	N.D.	N.D.	N.D.	N.D.
			Phosphogypsum (Setup F)			
Cd		50.0 \pm 1.4	4.44 \pm 0.1	N.D.	0.611 \pm 0.014	1.71 \pm 0.03
In		64 \pm 7	N.D.	N.D.	1.7 \pm 0.3	20 \pm 3
Sn		48.9 \pm 1.2	1.83 \pm 0.09	15.3 \pm 0.9	1.13 \pm 0.11	2.2 \pm 0.6
Pt		44 \pm 18	0.06 \pm 0.12	14 \pm 4	4 \pm 3	2.5 \pm 0.8

Table 4: Summary of interfering elements fractionation (%) for sediment and phosphogypsum samples. 3 replicates were performed per test. The results are shown as weighted averages \pm weighted uncertainty. Sup: Supernatant (after hydroxide precipitation, if any). Load: Elute obtained after loading U and Th in the resin. Wash and Cond. are the solutions collected after washing the resin and conditioning it to chloride form.

form.

Sample	^{238}U (α)	^{238}U (ICP)	$^{238}\text{U}/^{234}\text{U}$ (α)	$^{238}\text{U}/^{234}\text{U}$ (ICP)	^{232}Th (α)	^{232}Th (ICP)	$^{232}\text{Th}/^{230}\text{Th}$ (α)	$^{232}\text{Th}/^{230}\text{Th}$ (ICP)
F10, phosphate rock	694±11	637±9	0.999±0.016	1.003±0.011	11±1	7.70±0.24	0.0234±0.0022	0.0204±0.0010
CSN (phospho- gypsum)	55.0±1.7	57.2±1.0	0.98±0.03	0.949±0.004	6.1±0.1	3.80±0.06	0.0184±0.0005	0.0192±0.0006
T5 (sediment)	308±7	297±3	0.93±0.03	0.919±0.006	N.M.	24.3±0.4	N.M.	0.130±0.003
OT1 (sediment)	N.M.	90.0±0.8	N.M.	0.882±0.022	30.1±1.1	26.0±0.3	0.304±0.014	0.303±0.010

Table 5. Results obtained in the samples used for validation of the technique described in the text. CSN: Recommended values. N.M: Not measured. Activity concentration is expressed in Bq kg⁻¹. Isotope ratios are expressed as activity ratios.

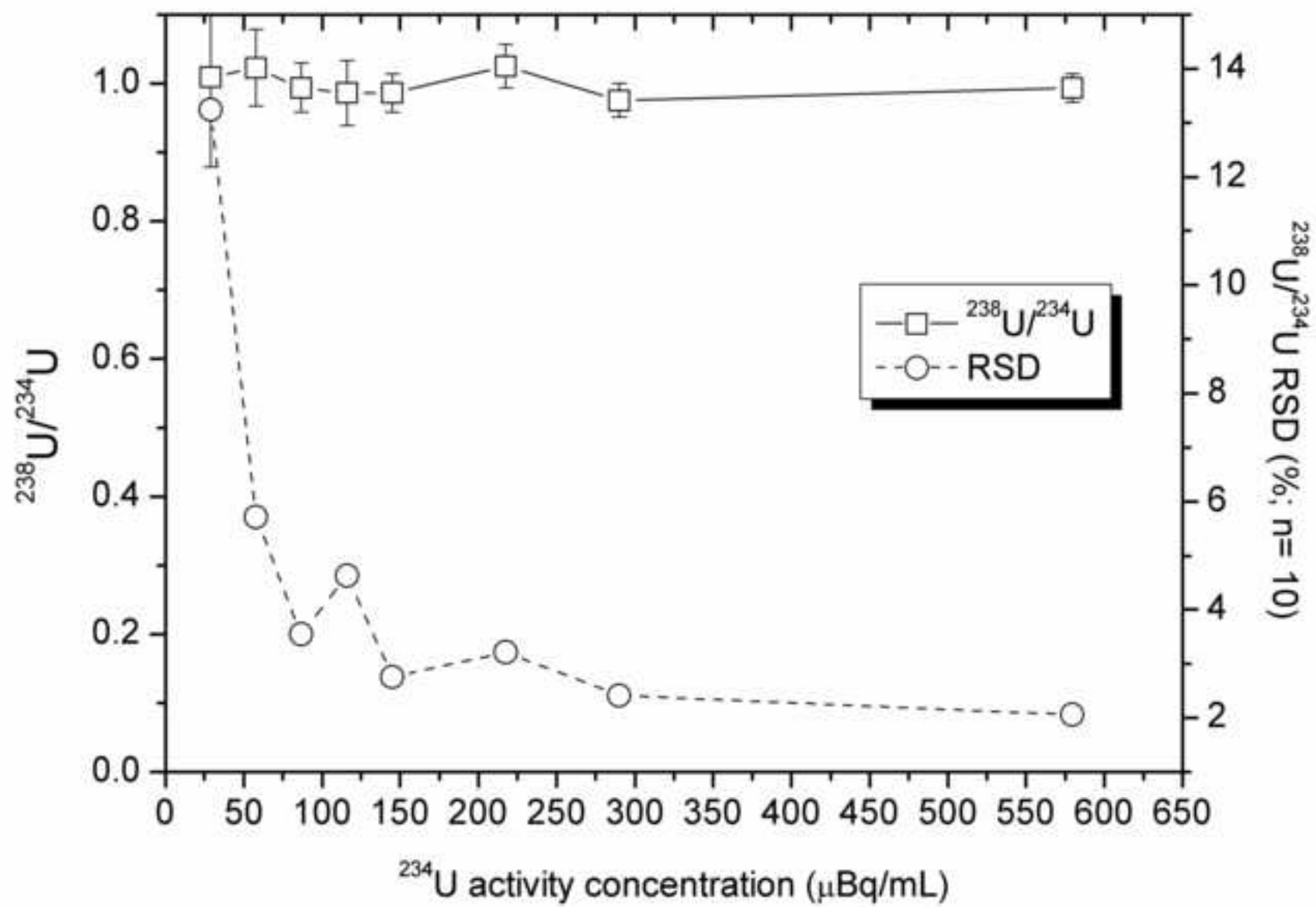
Sample	Cr ($\mu\text{g g}^{-1}$)	Ca (%)	Mn ($\mu\text{g g}^{-1}$)	Ni ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	As ($\mu\text{g g}^{-1}$)	Sr ($\mu\text{g g}^{-1}$)	Cd ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)
O3	53.8±1.1	1.21±0.09	264±5	27.0±0.6	1328±11	1163±10	364±3	121.0±1.6	3.72±0.04	399.8±2.7
O5	81.8±1.6	4.1±0.6	275±5	23.6±0.9	1718±25	1844±32	386±7	277±5	7.05±0.10	601±6.26
O6	105±9	5.9±0.9	241±22	23.6±2.2	3056±276	4547±408	964±87	481±43	18.1±1.6	1284±115
T4	16.6±0.4	1.03±0.08	67.0±1.2	9.2±0.5	756±17	406±9	299±4	51.3±1.7	2.46±0.08	365±12
T5	52.5±1.0	3.20±0.19	158±4	19.0±0.4	1940±20	1647±19	1082±15	406±4	6.16±0.13	1363±10
T6	91.1±1.9	6.13±0.7	207±4	23.7±0.4	24815±37	2414±36	1228±22	546±14	12.37±0.17	2105±21
OT1	53.1±0.8	1.98±0.14	377±3	27.6±0.3	1643±18	1558±17	393±4	158.8±1.9	1.88±0.07	568±7
OT3	22.56±0.20	4.37±0.12	174.8±2.2	9.9±0.4	316±6	435±10	78.7±1.5	395±6	0.77±0.06	110.2±1.9
F06	30.9±0.4	N.M.	0.83±0.03	1.24±0.06	7.0±0.6	18.4±0.7	18.7±0.4	555±6	2.66±0.06	4.37±0.05
F10	90.1±1.4	N.M.	37.1±0.8	6.94±0.11	9.96±0.22	87.5±1.5	15.1±0.3	348±4	37.1±0.7	3.50±0.17
F17	15.72±0.16	N.M.	0.80±0.06	2.07±0.21	6.50±0.13	39.5±0.7	8.3±0.3	574±5	2.78±0.06	2.51±0.12
F18	11.19±0.16	N.M.	1.00±0.03	0.53±0.12	3.75±0.05	29.7±0.5	1.79±0.06	573±7	1.99±0.12	7.7±0.16
CSN	21.1±0.4	N.M.	1.48±0.11	41.2±0.6	4.98±0.07	14.78±0.25	1.92±0.11	549±5	2.34±0.04	6.51±0.07

Table 6. Results obtained in the phosphogypsum and sediment leachates analysed in this work. The sediment samples were collected at Odiel river ("O" samples), Tinto river ("T" samples) and at the confluence of both rivers ("OT" samples). Samples F06, F17, F18 and CSN are phosphogypsum samples, while F10 is a phosphate rock sample.

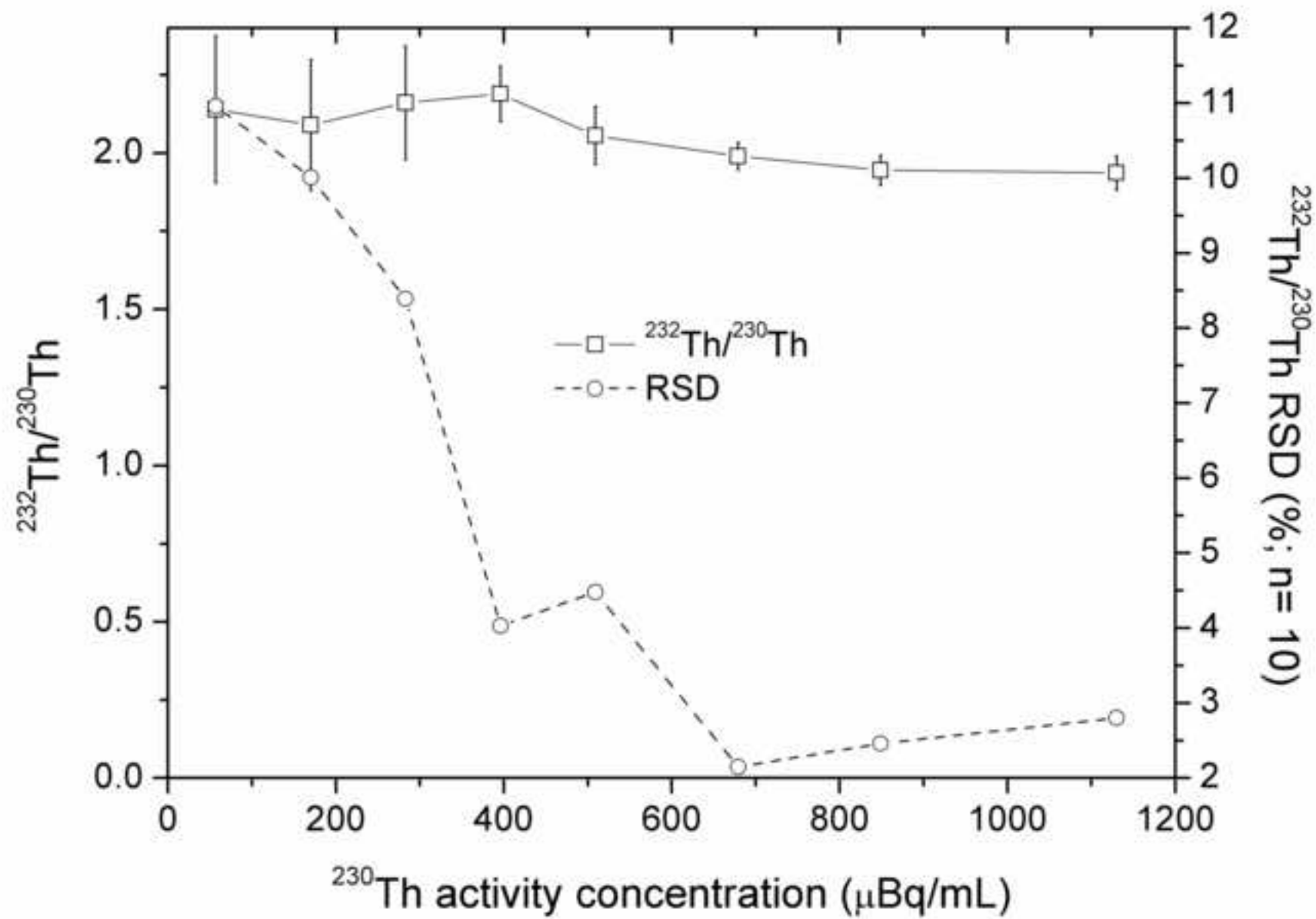
Sample	^{238}U (Bq/kg)	$^{238}\text{U}/^{234}\text{U}$	^{232}Th (Bq/kg)	$^{232}\text{Th}/^{230}\text{Th}$
O3	138.7±0.9	0.894±0.011	26.6±1.1	0.184±0.007
O5	320±5	0.934±0.006	36.0±0.9	0.0829±0.0011
O6	482±43	0.941±0.009	81±7	0.1260±0.0017
T3	129±2	0.919±0.021	15.75±0.16	0.486±0.016
T4	53.4±1.5	0.871±0.007	9.39±0.19	0.397±0.008
T6	476±6	0.941±0.005	31.2±0.5	0.130±0.003
OT3	36.2±0.8	0.96±0.03	7.77±0.04	0.204±0.003
F06 (PG)	611±14	0.970±0.006	11.8±0.3	0.01152±0.00020
F10 (PR)	637±9	1.003±0.011	7.70±0.24	0.0204±0.0010
F17 (PG)	250±3	0.962±0.009	14.6±0.3	0.0212±0.0004
F18 (PG)	189±3	0.960±0.015	13.28±0.12	0.0186±0.0005
CSN (PG)	57.2±1.0	0.949±0.004	3.80±0.06	0.0192±0.0006

Table 7: Results obtained in the sediment, phosphogypsum (PG) and phosphate rock (PR) samples used in this work. Isotope ratios are expressed as activity ratios.

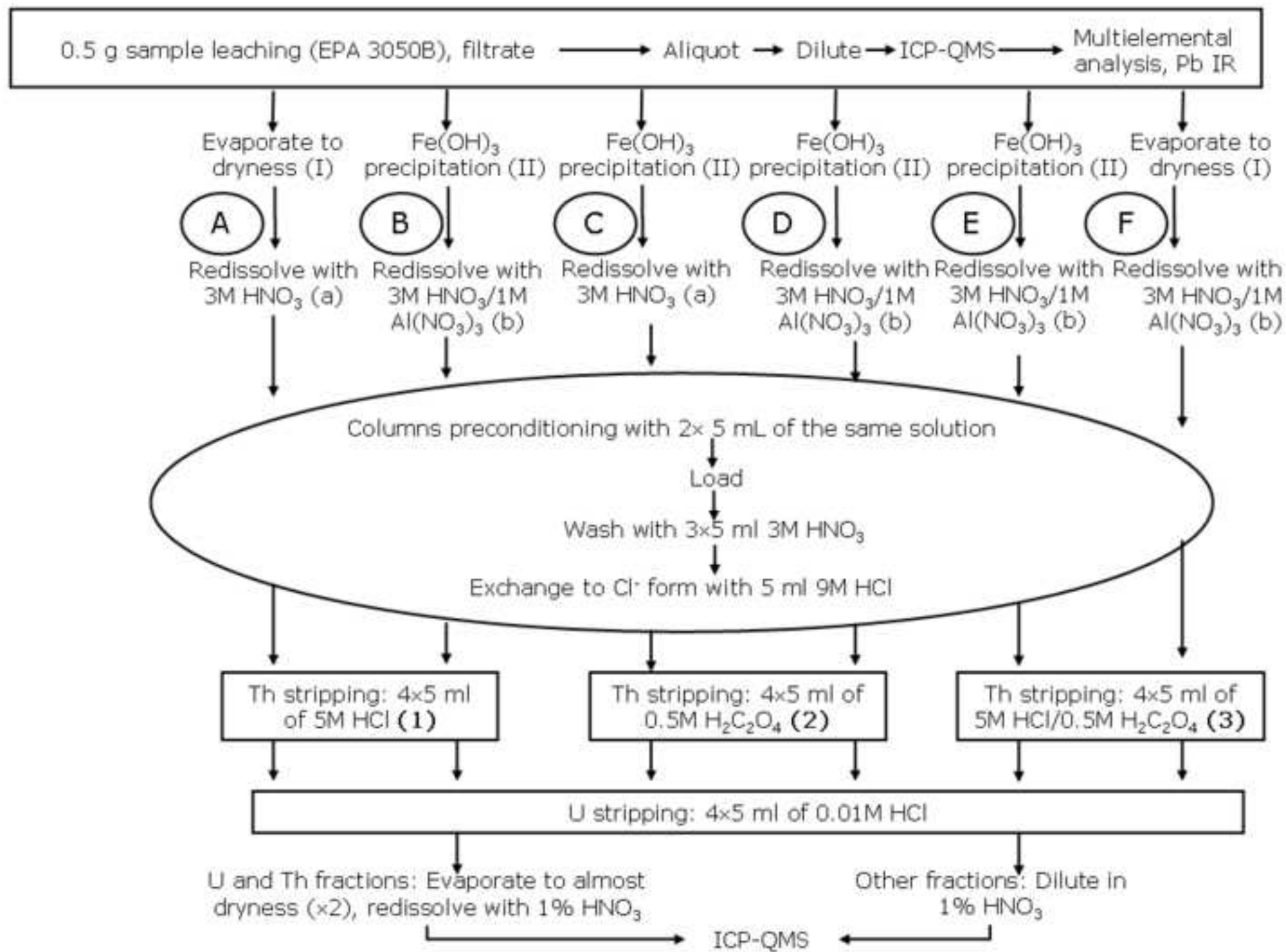
Figure(s)



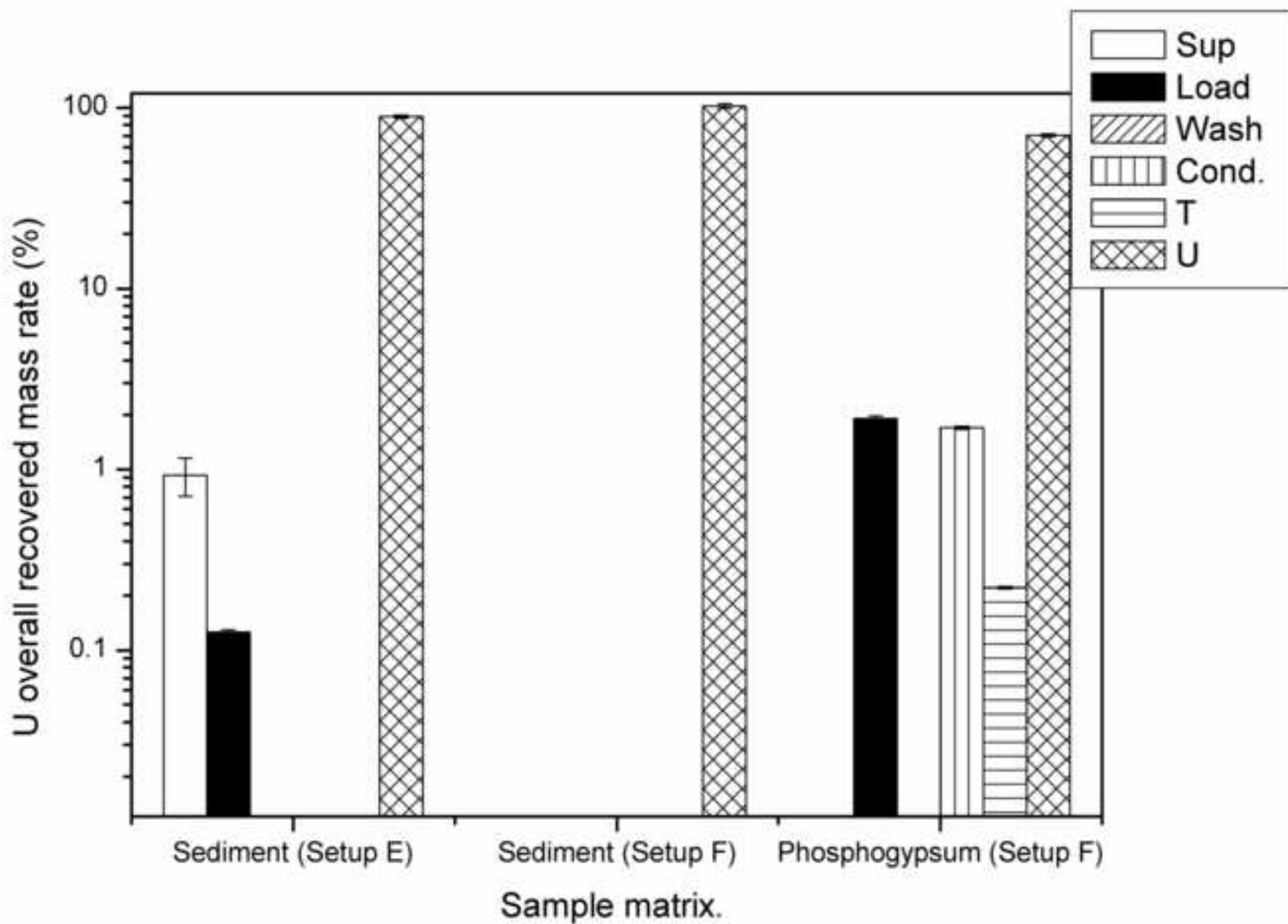
Figure(s)



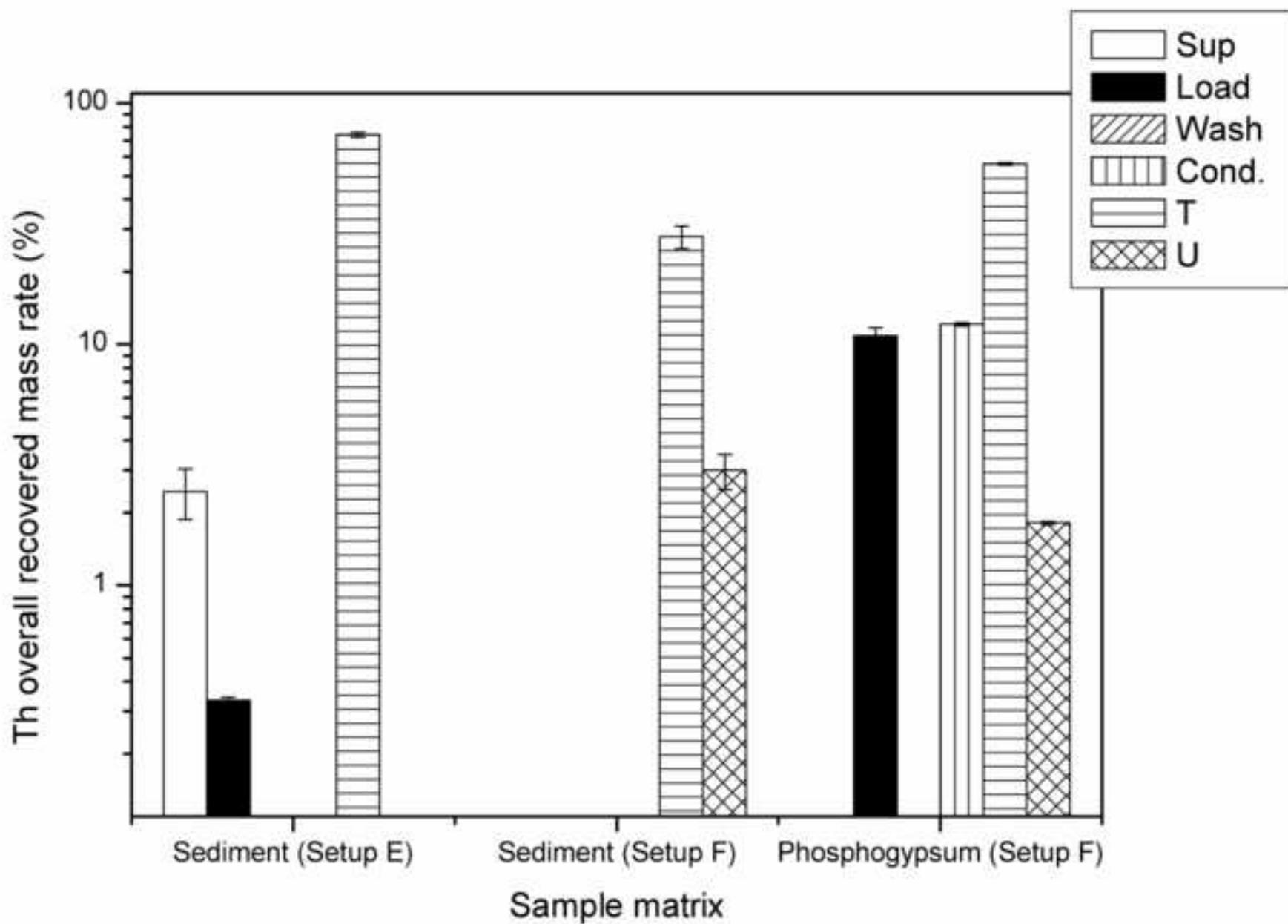
Figure(s)



Figure(s)



Figure(s)



Figure(s)

