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Thorium content in soil, water and sediment samples and fluvial sediment-associated transport in a catchment system with a semiarid-coastal interface, Brazil

--Manuscript Draft--

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Abstract:	Thorium (Th) is one of the main sources of natural radiation to ecosystems. However, data regarding Th concentrations in rocks, soil, water and sediments are currently scarce. Accordingly, this study aimed to establish background concentrations and quality reference values (QRVs) for Th in the environmentally impacted Ipojuca River catchment in Brazil, where the weathering of granites releases Th into the environment. Additionally, the study aimed to calculate Th fluxes in water, and both bed and suspended sediment. The mean Th concentration in the study catchment soils was 28.6 mg kg-1. The QRV for Th was estimated to be 21 mg kg-1 and 86.3 Bq kg-1. Bed and suspended sediment-associated concentrations ranged from 2.8 to 32.9 mg kg-1. Suspended sediment-associated discharge (3.42 t year-1) accounted for more than 99% of the total Th flux, whilst the dissolved phase transport was negligible in comparison. At the downstream cross section in the study catchment, suspended sediment samples exhibited Th concentrations similiar to those observed in rivers impacted by mining activities. The discharge of sediment to the ocean from the study area is mainly triggred by soil erosion processes in the anomaly region (middle-inferior course). It is essential to identify Th hotspots before establishing environmental policies regarding human health and environmental protection.
Response to Reviewers:	Dear Dr. Philippe Garrigues, Editor Environmental Science and Pollution Research, Dear Editor Please find enclosed a revised version of manuscript “Thorium content in soil, water

and sediment samples and fluvial sediment-associated transport in a catchment system with a semiarid-coastal interface, Brazil". We are very grateful for the helpful and constructive review comments. We have revised the draft paper on the basis of the review comments and our detailed responses to the comments are itemized (in blue) below.

Sincerely,
Prof. Yuri Jacques A. B. Silva (corresponding author)
Rodovia municipal Bom Jesus – Viana, km 01 – Planalto Horizonte, Bom Jesus
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Reviewers' comments:

Reviewer #1: The manuscript presents the results of a study aimed to establish background concentrations and quality reference values of thorium in the environmentally impacted river catchment in western Brazil. The manuscript is well-structured and of interest for journal readers. Some minor amendments are needed before publication.

Lines 157-160. The details on calculation of Th specific activities from 232Th mass concentrations should be provided.

Response: The specific Th activities were calculated using the conversion factor provided by the Central Laboratory of Radiological Protection of Poland (Malczewski et al. 2004), on the basis of the mass concentration of 232Th, assuming this species has a natural radioactive equilibrium and is an integral part of the elementary chemistry of Th.

This is now clarified to readers on ln 150-153 of the revised m/s with changes marked. The full reference details for the Malczewski et al. (2004) paper were already in the original m/s – see ln 388-390 in the revised m/s with changes marked.

Results and discussion - this sections should be strengthened by discussion of the results in the light of geological settings of the area which is given in Fig. 1. The comparison of the obtained results for Th concentrations with those obtained in other areas worldwide (Table 1) should also be amended with comparison of geological settings of studied area with those of areas for which comparison was made.

Response: We completely understand your concern in this regard. Please note that we added a soil map and a revised and more informative geological figure (the revised Figure 1) as per below:

Fig. 1 Location of the Ipojuca catchment in Brazil, geology, soil classes and the distribution of soil and sediment sample collection points in the upstream and downstream sites.
Additionally, to address this specific review comment, we are now only comparing Th concentrations among soils derived from granites and gneisses and added the global average value (UNSCEAR 2000) in a revised Table 1:
Table 1 Average Th concentrations (mg kg−1) in soils of the Ipojuca watershed compared to existing international soil data.
CountriesTh content (mg kg-1)
This study28.5
Brazil (Savanna biome)112
France25.9
Indian36.9
Malaysia480
Spain517.7
Worldwide67.4
1Marques et al. (2004); 2Aubert et al. (2004); 3Braun et al. (2018); 4Sanusi et al. (2017); 5Taboada et al. (2006); 6UNSCEAR (2000).

Aiming to improve the discussion, the following paragraphs were rewritten or added:

The revised comparison is now discussed on ln 159-164 in the revised m/s with

changes marked:
‘The background concentrations of Th in soils ranged from 13.2 to 72.3 mg kg-1, with an average of 28.6 mg kg-1. Such values are higher than those reported for soils derived from granite (Aubert et al. 2004; Taboada et al. 2006) and gneiss (Marques et al. 2004; Braun et al. 2018) worldwide (Table 1). Moreover, Th concentrations in soils from the Ipojuca watershed were higher than the average concentrations reported for soils under coal exploration (9.9 mg kg-1; Hussain et al. 2018), impacted by uranium tailings (15.1 mg kg-1; Yan and Luo 2014), and affected by mining operation (12.8 mg kg-1; Momčilović et al. 2013)’.

Additional new text has also been added on ln 175-187 of the revised m/s with changes marked to extend the discussion of the study data:
The QRVs for Th in soils of the Ipojuca watershed were 21 mg kg-1 for mass concentration and 86.3 Bq kg-1 for specific activity; Th specific activity was about three fold higher than the corresponding estimate value (30 Bq kg-1) reported for worldwide soils (UNSCEAR, 2000) and similar to mining soils in Brazil (90.8 Bq kg-1; Peixoto et al. 2016).
Spatial variability of Th in soils (Fig. 2) showed a hotspot in lower middle regions of the watershed. Thorium concentrations in the hotspot at the downstream sites ranged from 24 to 72 mg kg-1. Accordingly, this watershed area supplies a significant part of the total Th exported to the coastal zone. These hotspots are probably due to the abundance of monazite- and zircon-enriched granites (Figure 3a and 3b) with high Th concentration, i.e., 10% (Fig. 3a) and 28-42% (Table 2), respectively. Thorium is depleted in most rocks, but it can replace chemically closely related elements such as rare earth elements in some rocks (Taboada et al. 2006; Breiter et al. 2014; Kirkland et al. 2015). The downstream catchment sites are intensely weathered, but even recalcitrant minerals such as monazite and zircon might supply thorium. The low and high ZrO2 concentration at upstream and downstream sites (Fig. 2) confirm this behaviour.
Additionally, a new Table 2 and corresponding text has been added – see ln 237-245 in the revised m/s with change marked:

Table 2 Elemental composition of minerals in metaluminous and peraluminous granites in the Ipojuca watershed, Brazil, using a scanning electron microscope with energy-dispersive X-ray spectroscopy attached facilities (SEM-EDS)
MineralCePLaNdThPrSmSiFeCaZrUAlKTi
Peraluminous granite (%)
Monazite34.017.016.011.010.04.03.02.01.51.5-----
Zircon3.07.0-2.542.0--11.0-17.09.06.01.00.5-
Metaluminous granite (%)
Zircon11.06.54.53.528.0- - 9.51.011.019.0- 1.00.51.0

‘Soils easternly located (n = 13) commonly exhibit Th enrichment with an increase in ZrO2 (0.49) (p<0.1) and a decrease in SrO (-0.69) (p<0.01), respectively (Fig. 2), while soils in the western parts (n = 12) exhibited Th enrichment with increasing Fe2O3 (0.79) (p<0.01), TiO2 (0.67) (p<0.05), Fe (0.83) (p<0.01), Mn (0.58) (p <0.05) and SrO (-0.74) (p <0.01) depletion. Similar behaviour has been reported previously (Du et al. 2012; Négrel et al. 2018; Hussain et al. 2018)’.

Finally, we inserted revised discussion on ln 262-268:
The mean soil Th concentrations were higher than in sediment samples at both cross sections (Figure 4). This finding suggests that Th originated mainly from weathering processes Thorium concentration in suspended sediments was positively correlated with Fe at the upstream (0.62, p<0.01) and downstream (0.66, p<0.05) cross sections as well as with Mn at both the upstream (0.63, p<0.05) and downstream (0.79, p<0.01) sections. Furthermore, Th concentration in the bed sediment samples showed positive correlations with Fe (0.91) and Mn (0.66) at the downstream cross section, p<0.01 and p<0.05, respectively. Silva et al. (2015a) reported similar behaviour among Fe and various trace elements (Pb, Cr, Cu, Ni, Hg, As).

Reviewer #2: Report on the REVIEW OF THE MANUSCRIPT ESPR-D-19-03074 with the title "Thorium content in soil, water and sediment samples and fluvial sediment-associated transport in a catchment system with a semiarid-coastal interface, Brazil" submitted to ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH.

This document reports a study at watershed level aiming at (i) establishing background concentrations and quality reference values for Thorium and (ii) and estimate Thorium fluxes in the river. Soil samples have been collected in 25 sites; an unknown number of "granite" samples have been collected and analysed and Th flux have been measured in two river sections.

In short, the manuscript is fragile, especially taking into account the objectives proposed.
The dataset, and the text, figures and tables are not fully adequate for the purpose, showing too many drawbacks, omissions and inconsistencies, namely in Materials and Methods; and often with a vague inaccurate writing, with lack of scientific objectivity. Namely:

(i) The soil dataset shown here seems to have been produced over adequate sampling procedures at site level. However the number of samples (25), their distribution and the lack of sampling duplicates makes this dataset hardly adequate for a good spatial characterization of the thorium concentrations in the soil of the catchment. Namely, the number of samples is too small for a robust statistical analysis, and the soil sampling sites do not adequately cover the study area, as they are always too much along the main river, giving the impression that the sites were planned for stream sediments sampling rather than soil sampling In case the samples have been collected under a larger (e.g.: regional / state / national ambit) multipurpose geochemical project, then, it should be referred;

Response: Please note that a total of 25 composite soil samples consisting of four subsamples (i.e. 100 sub samples along the basin) were taken from twenty-five sampling sites under native vegetation (i.e., with no anthropogenic influence) at 0–20 cm depth in order to represent the diversity of soil classes and soil parent materials. These samples cover all sites under no or minimal anthropic influence. We ruled out some additional potential sampling sites due to evidence of anthropogenic influence and we would therefore like to emphasize the low occurrence of sites under fully preserved referenced conditions. On this basis, we feel that our sampling strategy was pragmatic.

(ii) the lithology of the catchment is provided, shown with perhaps too much detail (20 lithologies while only 25 soil samples!) in Figure 1, but not explained in terms of geological terranes, that is, whether and how close they are genetically related;
Response: We have completely revised the original Figure 1 – see new Figure 1 in the revised m/s with changes marked.

(iii) soil types (and respective percentage cover) are mentioned and two climatic zones are referred, but in both cases their likely geographical boundaries are not shown;

Response: Please see the new figure 1 in the revised m/s with changes marked.

(iv) granite samples are mentioned, but number, location of the actual sampling sites and the actual granite type are not referred nor shown in a map;

Response: Please see the new Figure 1 below and in the revised m/s with changes marked which now shows the location of the rock sampling sites and specifies the granitoid types in the legend.

Fig. 1 Location of the Ipojuca catchment in Brazil, geology, soil classes and the distribution of soil and sediment sample collection points in the upstream and downstream sites.

In support of the revised Figure 1, new text is now found on ln 87-89 of the revised m/s with changes marked:

“Soil parent materials are mainly metaluminous granitoid (56%), orthogneiss (31%), and biotite-muscovite gneiss (8%) (Silva et al. 2015b) (Fig. 1). Soils in the catchment are predominantly Entisols (37%), Ultisols (32%), and Alfisols (18%)”.

(v) the Th fluxes were determined in two cross sections for which the coordinates are given, but their actual location in a map is not shown;

Response: Please note that the locations have been added to the revised Figure 1 – see revised m/s with changes marked.

(vi) the soil samples are not listed in a table and the soil type, geology and climate are not assigned to each one of them; also, the other sampled materials (sediment, water and rock) are not adequately reported;

Response: Thank you for your suggestion. Please note that we added a soil map and climate information (demarcation of semi-arid and humid zones) n in the revised Figure 1 – see revised m/s with changes marked. In support of these changes, we added the following text on ln 85-87 of the revised m/s with changes marked:

"Average annual rainfall ranges from 600 mm in the semiarid, western region to 2400 mm in the coastal zone while annual average air temperature are 25 ºC and 28 ºC, respectively (Condepe/Fidem 2005)".

(vii) the analytical methods used, namely the samples' digestion, are questionable for the purpose, or at least, its use should be discussed in the manuscript, as the main thorium source is likely to be the resistate minerals, such as zircon, which hardly digest with the acid solution used; thus thorium concentrations and thorium specific activities are likely to be higher than the reported values;

Response: We understand the comment raised by the reviewer here. In fact, the method we deployed is not intended to accomplish total decomposition of the sample. In contrast, the method we used extracts the Th that is most likely to become available in the medium and long term (Alloway, 2013). This extraction is considered to represent the most environmentally relevant fraction (carbonates, sulphates, oxides and less labile phases) (USEPA, 1998; Löll et al. 2011). Thus, it does not extract the Th strongly bound to the silicate minerals. We therefore feel strongly that our method is applicable to determine Th in soils when one has an environmental concern as we do. Note that we are looking for background concentrations and quality reference values for future regulations on Th in soils. Most regulations do not consider total concentration (using HF), but, instead, environmentally available concentrations (using HCl and HNO3). In addition, the German Soil Protection Regulation (BBodSchV, 1999) recommends extraction using aqua regia (HCl, HNO3, 3:1) for estimating the "soil–human" exposure pathway.

On this basis, we edited the original text – see ln 124-127 in the revised m/s with changes marked:

'This method extracts the levels of Th that will probably become available in the medium and long term (Alloway 2013). In addition, the German Soil Protection Regulation (BBodSchV, 1999) and the Brazilian legislation (CONAMA, 2009) recommend extraction using HCl and HNO3 (3:1) for estimating the "soil–human" exposure pathway'.

The full reference details for the Alloway (2013) citation are now provided in the revised m/s on ln 322-323. The full reference detials for the BBodSchV (1999) are now in the revised m/s with changes marked on ln 337-339. The detials for CONAMA (2009) are now included on ln 344-345.

(viii) the rationale for the list of elements and other parameters analysed together with Thorium (Th, Fe and Mn by ICP-OES after acid digestion, and "total" TiO2, Fe2O3, SrO and ZrO2 by XRF, plus LoI and pH) is not provided, and LoI is referred in materials and methods but not mentioned in the results and discussion;

Response: Please see below and in the revised m/s on ln 130-137 that we added the detection limits of elements determined in ICP and FRX. In addition, we also added into the revised m/s the variation of the loss on ignition data:

Calibration was carried out every ten samples and analysis was done only when the coefficient of determination (R2) of the calibration curve was higher than 0.999. Whenever more than 10% deviation was observed, the equipment was recalibrated and samples reanalyzed. All analyses were performed in duplicate. Concentrations of Th, Fe, and Mn were determined by ICP-OES. The detection limits (mg kg−1) were 0.01 for Th, 0.341 for Fe, and 0.005 for manganese. Recovery rates of the standard reference material were as follows (%): Th (94); Fe (93); Mn (85). Total TiO2, Fe2O3, SrO and ZrO2 concentrations were determined using XRF spectrometry (S8 TIGER ECO – WDXRF-1KW). Loss on ignition was determined at 1000 °C ranged from 1.1 to 4.7%. Detection limits (%) for TiO2, Fe2O3, SrO, and ZrO2 were 0.003, 0.1, 0.009, and 0.007, respectively.

(ix) the analytical results for soil, sediment and water samples are not shown in a table; the values reported in the caption of Figure 2 for the SEM-EDS granite samples should be shown in a table instead; and an adequate table of summary statistics for each sampled material should also be produced and shown;

Response: Thank you for your suggestion. We added a new Table 2 in the revised m/s with changes marked:

Table 2. Elemental composition of minerals in metaluminous and peraluminous granites in the Ipojuca watershed, Brazil, using a scanning electron microscope with energy-dispersive X-ray spectroscopy attached facilities (SEM-EDS)
MineralCePLaNdThPrSmSiFeCaZrUAlKTi
Peraluminous granite (%)
Monazite34.017.016.011.010.04.03.02.01.51.5-----
Zircon3.07.0-2.542.0--11.0-17.09.06.01.00.5-
Metaluminous granite (%)
Zircon11.06.54.53.528.0- - 9.51.011.019.0- 1.00.51.0

Additionally, please note below and in the manuscript that we added new text (ln 179-187) in support of the new Table 2:

‘Spatial variability of Th in soils (Fig. 2) showed a hotspot in lower middle regions of the watershed. Thorium concentrations in the hotspot at the downstream sites ranged from 24 to 72 mg kg-1. Accordingly, this watershed area supplies a significant part of the total Th exported to the coastal zone. These hotspots are probably due to the abundance of monazite- and zircon-enriched granites (Figure 3a and 3b) with high Th concentration, i.e., 10% (Fig. 3a) and 28-42% (Table 2), respectively. Thorium is depleted in most rocks, but it can replace chemically closely related elements such as rare earth elements in some rocks (Taboada et al. 2006; Breiter et al. 2014; Kirkland et al. 2015). The downstream catchment sites are intensely weathered, but even recalcitrant minerals such as monazite and zircon might supply thorium. The low and high ZrO2 concentration at upstream and downstream sites (Fig. 2) confirm this behaviour’.

(x) the method used for the production of the maps with the distribution and the probability of exceedance (not explained!!) of Th concentrations in soil are not explained and its use is, at least, highly questionable due to the linearity of the sampling sites;

Response: Yes, we agree with your observation here. We believe that the number of soil samples is not enough to show the distribution and the probability of exceedance. Thus, we deleted the original figure and added a new one in order to show the Th and Zr concentrations using the subdivision of Jenks natural breaks (five categories) – see revised Figure 2 in the revised m/s with changes marked:

Fig. 2 Spatial distribution of the background concentrations of Th and ZrO2 in the Ipojuca watershed in Brazil.

The following new text (ln 179-187) was added in support of the new Figure 2:
‘Spatial variability of Th in soils (Fig. 2) showed a hotspot in lower middle regions of the watershed. Thorium concentrations in the hotspot at the downstream sites ranged from

24 to 72 mg kg-1. Accordingly, this watershed area supplies a significant part of the total Th exported to the coastal zone. These hotspots are probably due to the abundance of monazite- and zircon-enriched granites (Figure 3a and 3b) with high Th concentration, i.e., 10% (Fig. 3a) and 28-42% (Table 2), respectively. Thorium is depleted in most rocks, but it can replace chemically closely related elements such as rare earth elements in some rocks (Taboada et al. 2006; Breiter et al. 2014; Kirkland et al. 2015). The downstream catchment sites are intensely weathered, but even recalcitrant minerals such as monazite and zircon might supply thorium. The low and high ZrO2 concentration at upstream and downstream sites (Fig. 2) confirm this behaviour'.

(xi) the statistical analysis of the data is poor and using questionable methods. The concept of the probability of exceedance of the quality reference values is interesting and should be further explained an explored;

Response: Thank you for your suggestion. We decided to remove the kriging and to add the point distribution map of the concentrations of Th in the sampled locations, using the subdivision of Jenks natural breaks (five categories) – see revised Figure 2 in the revised m/s with changes marked.

(xii) the values from the present work are compared with data from many other works, which is good. However, it needs to be less random, with more focus on similar examples, namely granite type / mining areas in Brazil and any other parts of the globe (ex.: SW England, Sweden, Portugal, France, China, Africa, North America, etc..), tha have been analysed using similar lab methods and assuring that the statistic parameters being compared are the same (e.g.: the arithmetic mean, median and geometric mean are not the same, and should not be directly compared!);

Response: We edited the draft m/s and now we are only comparing Th concentrations among soils derived from granites and gneisses. In addition, we added the corresponding global average value (UNSCEAR 2000) – see revised Table 1; also we used a common statistical parameter for comparison (i.e. the mean).

Table 1 Average Th concentrations (mg kg−1) in soils of the Ipojuca watershed compared to existing international soil data.

Countries	Th content (mg kg-1)
This study	28.5
Brazil (Savanna biome)1	12
France2	5.9
Indian3	6.9
Malaysia4	80
Spain5	17.7
Worldwide6	7.4

1Marques et al. (2004); 2Aubert et al. (2004); 3Braun et al. (2018); 4Sanusi et al. (2017); 5Taboada et al. (2006); 6UNSCEAR (2000).

The following revised text discusses the new Table 1 – see ln 159-164 in the revised m/s with changes marked:

'The background concentrations of Th in soils ranged from 13.2 to 72.3 mg kg-1, with an average of 28.6 mg kg-1. Such values are higher than those reported for soils derived from granite (Aubert et al. 2004; Taboada et al. 2006) and gneiss (Marques et al. 2004; Braun et al. 2018) worldwide (Table 1). Moreover, Th concentrations in soils from the Ipojuca watershed were higher than the average concentrations reported for soils under coal exploration (9.9 mg kg-1; Hussain et al. 2018) , impacted by uranium tailings (15.1 mg kg-1; Yan and Luo 2014), and affected by mining operation (12.8 mg kg-1; Momčilović et al. 2013)'.

(xiii) the discussion is also poor, with parametric statistics, such as the arithmetic mean and the Pearson correlation being abusively and inconsistently used, while the number of samples for each case is not shown in Table 2;

Response: Thank you for your suggestion. We have replaced Pearson with a Spearman correlation due to the lack of normal distributions. We also decided to remove the correlations referring to the hotspot area due to the insufficient number of soil samples. Please note that we added the number of observations and included the corresponding statistical results in the revised text on ln 241-245:

‘Soils easternly located (n = 13) commonly exhibit Th enrichment with an increase in ZrO_2 (0.49) ($p<0.1$) and a decrease in SrO (-0.69) ($p<0.01$), respectively (Fig. 2), while soils in the western parts (n = 12) exhibited Th enrichment with increasing Fe_2O_3 (0.79) ($p<0.01$), TiO_2 (0.67) ($p<0.05$), Fe (0.83) ($p<0.01$), Mn (0.58) ($p <0.05$) and SrO (-0.74) ($p <0.01$) depletion. Similar behaviour has been reported previously (Du et al. 2012; Négrel et al. 2018; Hussain et al. 2018)’.

And on ln 262-268:

‘The mean soil Th concentrations were higher than in sediment samples at both cross sections (Figure 4). This finding suggests that Th originated mainly from weathering processes Thorium concentration in suspended sediments was positively correlated with Fe at the upstream (0.62, $p<0.01$) and downstream (0.66, $p<0.05$) cross sections as well as with Mn at both the upstream (0.63, $p<0.05$) and downstream (0.79, $p<0.01$) sections. Furthermore, Th concentration in the bed sediment samples showed positive correlations with Fe (0.91) and Mn (0.66) at the downstream cross section, $p<0.01$ and $p<0.05$, respectively. Silva et al. (2015a) reported similar behaviour among Fe and various trace elements (Pb, Cr, Cu, Ni, Hg, As)’.

(xiv) The comparison of Th concentrations in soil and sediment loads is poor. It does not mention the differences in grainsize, and the (high) content in the study area of resistate thorium host minerals, such as zircon and monazite, is not adequately explored (for instance, using elements' ratios) aiming for a better understanding of the Th partition between soil and sediments;

Response: Thorium concentration in soils was higher than those observed for suspended sediments. We recognise this as a possible limitation of the study but it would be a problem if we had observed the highest Th concentrations in suspended sediments. In Brazil, a national regulation developed to establish QRVs in soils (CONAMA 2009) requires the use of < 2-mm fraction for soil. So, we understand that even if we compare the same grainsize, the concentration in soils would keep the highest one not changing our discussion. Please note that DH-48 sampler collects only silt and clay fractions and there is no remaning sample due to the difficulty linked to the suspended sediment sampling in rivers. We would have separated the silt and clay fraction in soil samples if we had observed the highest Th concentration in suspended sediments. We agree that this is an importante point but in our study it will not change the discussion. We strongly believe that soil will keep showing the highest concentration.

(xv) Despite of some good references reported, the introduction needs much more information about thorium, namely about its isotopes, sources, chemistry and behaviour in the surface environment (namely in soil and water), and any biological interactions and exposure routes. Note that Th bio-geo-chemistry is quite different from that of Uranium and other elements more often included in environmental studies, such as, As, Cd, Cr, Cu, Pb, Sn, Zn, etc.. Also, its use by man is clearly not comparable yet. But i agree that assessing the natural background for Th or, at least, assessing its baselines, is a fundamental task. Man always impact the environment wherever they go or do... but in what extent the referred industrial complex (what do they do??), or the sugarcane, or the lack of sanitation, can turn thorium into an environmental concern? The levels of pollution allegedly reported for Pb and Zn in previous studies (in Introduction) cannot be simply implicitly 'extrapolated' to Th.

Response: We thank the reviewer for recognising that greater understanding of Th context and fluxes is a current research gap for filling. To address the review comment here, the following paragraph was added to the revised m/s with changes marked on ln 52-56:

The following paragraph was added: “The primary anthropogenic Th sources are mining, milling, and processing operations. The use of phosphate fertilizers has also been one of the factors responsible for Th inputs into catchment soils and waters (Mazzilli et al. 2000; Salute and Mazzilli 2006; Conceição et al. 2009; Servitzoglou et al. 2018). Thorium has been used in small amounts as a replacement to uranium in nuclear reactor fuels (Xiao et al. 2016), which has increased Th environmental exposure".

In addition, the following sentence was added on ln 67-71 of the revised m/s with changes marked

'This catchment encompasses various potentially environmentally-threaten activities, including a port industrial complex (Suape) that ships over eleven million tons of chemical products and vast areas under sugarcane cultivation. Along with Suape complex, Ipojuca catchment surroundings have faced an industrial and urban development that puts additional pressure on the environment (Silva et al. 2015b)'.

The full reference details for Silva et al. (2015b) have been added to the revised reference list on ln 439-441.

The following original sentence was deleted: "The lack of urban sanitation in most municipalities along its watercourse is another cause of negative environmental impacts that requires monitoring". "The lack of sanitation is not expected to be an important Th source"

The consistency of the background values and of the quality reference values is, thus, questionable, and the quality of the writing do not help overcoming this issue.
Given the issues raised above, I suggest the authors to address them as much as possible, namely:
(a) taking time in improving the Materials and Methods, with a clear structure and a clear focused text, thoroughly addressing sampling and analysis for each material (soil, bed and suspended sediment, water, granite samples), and clearly pointing out the related pros and cons of the materials and methods for the purpose; including an explanation about the list of elements and other parameters used;

Response: We have revised the Materials and Methods section – see edited text on ln 85-92, 104, 110, 115-117, 123-127, 130-137, 149 and 150-156.

(b) to adequately show the data and its stats in tables; rework the figures;
Response: We have revised Figures the original Figures 1 and 2 and the original Tables 1 and 2 – see revised m/s with cnanges marked.

(c) to attempt using auxiliary data, such as the geology / lithology, soil type, climatic zone (or meteorological data, if available), elevation (if easily available), human occupation, etc, to improve the interpolation of Thorium and its probability of exceedance across the area, aiming to overcome the problems mentioned above;

Response: We replaced the kriging in the original m/s with a new Figure 2:

Fig. 2 Spatial distribution of the background concentrations of Th and ZrO2 in the Ipojuca watershed in Brazil.

(d) to get informed about Compositional Data Analysis and its increasing use in environmental geochemistry, and to attempt using its principles, namely with the use of logratios and, perhaps, of multivariate techniques, aiming to improve the data analysis and the understanding of processes with thorium in the watershed under study; This will certainly allow to improve the discussion.

Response: We are grateful for the suggestion. We did not apply multivariate techniques such as principal component analysis or factor analysis because similar results were obtained using a simple correlation analysis. However, we agree that in some papers the main problem is the lack of recognition that the authors are dealing with compositional data and the biases this can create for correlations, FA and other statistical methods if closure effects are not removed. We have followed a simple correction method such as additive log ratios (alr-) or centred log ratios (clr-) in other manuscripts of our team which are very easy to calculate as shown by:
Tolosana-Delgado R., 2008. Compositional Data Analysis in a Nutshell, www.sediment.unigoettingen.de/staff/tolosana/extra/CoDaNutshell.pdf

	(e) the Dataset on its own may deserve to be published, but the authors need to show it very neatly, by clarifying the methods; adequately showing the study area, samples and results; improving the statistical analysis and better exploring the diversity of materials sampled and analysed; and bringing data limitations and advantages into the discussion; Response: the above details throughout the response to review clarify how we have addressed these comments here. (f) the text needs to be less vague, more focused and accurate, with a better scientific language in all its sections. I'm not sending suggestions on the PDF, as they would be too extensive. Response: We have revised the text on ln 52-56, 67-71, 85-92, 104, 110, 115-117, 123-127, 130-137, 149, 150-156, 159-164, 171-245, 262-268. We would like to thank the editor and anonymous reviewers for their insightful and constructive comments that greatly contributed to the improvement of the original manuscript.
Additional Information:	
Question	**Response**
§Are you submitting to a Special Issue?	No

Dear Dr. Philippe Garrigues,

Editor

Environmental Science and Pollution Research,

Dear Editor

Please find enclosed a revised version of manuscript "Thorium content in soil, water and sediment samples and fluvial sediment-associated transport in a catchment system with a semiarid-coastal interface, Brazil". We are very grateful for the helpful and constructive review comments. We have revised the draft paper on the basis of the review comments and our detailed responses to the comments are itemized (in blue) below.

Sincerely,

Prof. Yuri Jacques A. B. Silva (corresponding author)
Rodovia municipal Bom Jesus – Viana, km 01 – Planalto Horizonte, Bom Jesus
Piauí – PE Zip code: 64900-000
Brazil

Reviewers' comments:

Reviewer #1: The manuscript presents the results of a study aimed to establish background concentrations and quality reference values of thorium in the environmentally impacted river catchment in western Brazil. The manuscript is well-structured and of interest for journal readers. Some minor amendments are needed before publication.

Lines 157-160. The details on calculation of Th specific activities from 232Th mass concentrations should be provided.

Response: The specific Th activities were calculated using the conversion factor provided by the Central Laboratory of Radiological Protection of Poland (Malczewski et al. 2004), on the basis of the mass concentration of ^{232}Th, assuming this species has a natural radioactive equilibrium and is an integral part of the elementary chemistry of Th.

This is now clarified to readers on ln 150-153 of the revised m/s with changes marked. The full reference details for the Malczewski et al. (2004) paper were already in the original m/s – see ln 388-390 in the revised m/s with changes marked.

Results and discussion - this sections should be strengthened by discussion of the results in the light of geological settings of the area which is given in Fig. 1. The comparison of the obtained results for Th concentrations with those obtained in other areas worldwide (Table 1) should also be amended with comparison of geological settings of studied area with those of areas for which comparison was made.

Response: We completely understand your concern in this regard. Please note that we added a soil map and a revised and more informative geological figure (the revised Figure 1) as per below:

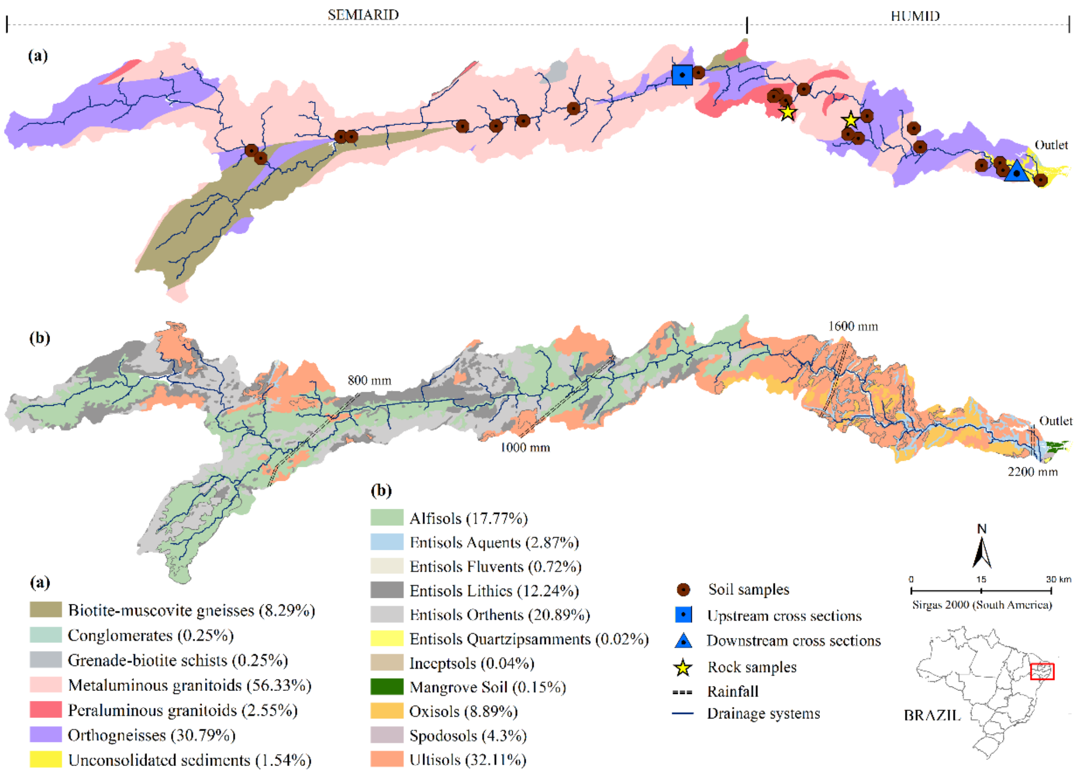

Fig. 1 Location of the Ipojuca catchment in Brazil, geology, soil classes and the distribution of soil and sediment sample collection points in the upstream and downstream sites.

Additionally, to address this specific review comment, we are now only comparing Th concentrations among soils derived from granites and gneisses and added the global average value (UNSCEAR 2000) in a revised Table 1:

Table 1 Average Th concentrations (mg kg^{-1}) in soils of the Ipojuca watershed compared to existing international soil data.

Countries	Th content (mg kg^{-1})
This study	28.5
Brazil (Savanna biome)[1]	12
France[2]	5.9
Indian[3]	6.9
Malaysia[4]	80
Spain[5]	17.7
Worldwide[6]	7.4

[1]Marques et al. (2004); [2]Aubert et al. (2004); [3]Braun et al. (2018); [4]Sanusi et al. (2017); [5]Taboada et al. (2006); [6]UNSCEAR (2000).

Aiming to improve the discussion, the following paragraphs were rewritten or added:

The revised comparison is now discussed on ln 159-164 in the revised m/s with changes marked:

'The background concentrations of Th in soils ranged from 13.2 to 72.3 mg kg^{-1}, with an average of 28.6 mg kg^{-1}. Such values are higher than those reported for soils derived from granite (Aubert et al. 2004; Taboada et al. 2006) and gneiss (Marques et al. 2004; Braun et al. 2018) worldwide (Table 1). Moreover, Th concentrations in soils from the Ipojuca watershed were higher than the average concentrations reported for soils under coal exploration (9.9 mg kg^{-1}; Hussain et al. 2018), impacted by uranium tailings (15.1 mg kg^{-1}; Yan and Luo 2014), and affected by mining operation (12.8 mg kg^{-1}; Momčilović et al. 2013)'.

Additional new text has also been added on ln 175-187 of the revised m/s with changes marked to extend the discussion of the study data:

The QRVs for Th in soils of the Ipojuca watershed were 21 mg kg^{-1} for mass concentration and 86.3 Bq kg^{-1} for specific activity; Th specific activity was about three fold higher than the corresponding estimate value (30 Bq kg^{-1}) reported for worldwide soils (UNSCEAR, 2000) and similar to mining soils in Brazil (90.8 Bq kg^{-1}; Peixoto et al. 2016).

Spatial variability of Th in soils (Fig. 2) showed a hotspot in lower middle regions of the watershed. Thorium concentrations in the hotspot at the downstream sites ranged from 24 to 72 mg kg^{-1}. Accordingly, this watershed area supplies a significant part of the total Th exported to the coastal zone. These hotspots are probably due to the abundance of monazite- and zircon-enriched granites (Figure 3a and 3b) with high Th concentration, i.e., 10% (Fig. 3a) and 28-42% (Table 2), respectively. Thorium is depleted in most rocks, but it can replace chemically closely related elements such as rare earth elements in some rocks (Taboada et al. 2006; Breiter et al. 2014; Kirkland et al. 2015). The downstream catchment sites are intensely weathered, but even recalcitrant minerals such as monazite and zircon might supply thorium. The low and high ZrO_2 concentration at upstream and downstream sites (Fig. 2) confirm this behaviour.

Additionally, a new Table 2 and corresponding text has been added – see ln 237-245 in the revised m/s with change marked:

Table 2 Elemental composition of minerals in metaluminous and peraluminous granites in the Ipojuca watershed, Brazil, using a scanning electron microscope with energy-dispersive X-ray spectroscopy attached facilities (SEM-EDS)

Mineral	**Ce**	**P**	**La**	**Nd**	**Th**	**Pr**	**Sm**	**Si**	**Fe**	**Ca**	**Zr**	**U**	**Al**	**K**	**Ti**
Peraluminous granite (%)															
Monazite	34.0	17.0	16.0	11.0	10.0	4.0	3.0	2.0	1.5	1.5	-	-	-	-	-
Zircon	3.0	7.0	-	2.5	42.0	-	-	11.0	-	17.0	9.0	6.0	1.0	0.5	-
Metaluminous granite (%)															
Zircon	11.0	6.5	4.5	3.5	28.0	-	-	9.5	1.0	11.0	19.0	-	1.0	0.5	1.0

'Soils easternly located (n = 13) commonly exhibit Th enrichment with an increase in ZrO_2 (0.49) ($p<0.1$) and a decrease in SrO (-0.69) ($p<0.01$), respectively (Fig. 2), while soils in the western parts (n = 12) exhibited Th enrichment with increasing Fe_2O_3 (0.79) ($p<0.01$), TiO_2 (0.67) ($p<0.05$), Fe (0.83) ($p<0.01$), Mn (0.58) ($p<0.05$) and SrO (-0.74) ($p<0.01$) depletion. Similar behaviour has been reported previously (Du et al. 2012; Négrel et al. 2018; Hussain et al. 2018)'.

Finally, we inserted revised discussion on ln 262-268:

The mean soil Th concentrations were higher than in sediment samples at both cross sections (Figure 4). This finding suggests that Th originated mainly from weathering processes Thorium concentration in suspended sediments was positively correlated with Fe at the upstream (0.62, $p<0.01$) and downstream (0.66, $p<0.05$) cross sections as well as with Mn at both the upstream (0.63, $p<0.05$) and downstream (0.79, $p<0.01$) sections. Furthermore, Th concentration in the bed sediment samples showed positive correlations with Fe (0.91) and Mn (0.66) at the downstream cross section, $p<0.01$ and $p<0.05$, respectively. Silva et al. (2015a) reported similar behaviour among Fe and various trace elements (Pb, Cr, Cu, Ni, Hg, As).

Reviewer #2: Report on the REVIEW OF THE MANUSCRIPT ESPR-D-19-03074 with the title "Thorium content in soil, water and sediment samples and fluvial sediment-associated transport in a catchment system with a semiarid-coastal interface, Brazil" submitted to ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH.

This document reports a study at watershed level aiming at (i) establishing background concentrations and quality reference values for Thorium and (ii) and estimate Thorium fluxes in the river. Soil samples have been collected in 25 sites; an unknown number of "granite" samples have been collected and analysed and Th flux have been measured in two river sections.

In short, the manuscript is fragile, especially taking into account the objectives proposed. The dataset, and the text, figures and tables are not fully adequate for the purpose, showing too many drawbacks, omissions and inconsistencies, namely in Materials and Methods; and often with a vague inaccurate writing, with lack of scientific objectivity. Namely:

(i) The soil dataset shown here seems to have been produced over adequate sampling procedures at site level. However the number of samples (25), their distribution and the lack of sampling duplicates makes this dataset hardly adequate for a good spatial characterization of the thorium concentrations in the soil of the catchment. Namely, the number of samples is too small for a robust statistical analysis, and the soil sampling sites do not adequately cover the study area, as they are always too much along the main river, giving the impression that the sites were planned for stream sediments sampling rather than soil sampling In case the samples have been collected under a larger (e.g.: regional / state / national ambit) multipurpose geochemical project, then, it should be referred;

Response: Please note that a total of 25 composite soil samples consisting of four subsamples (i.e. 100 sub samples along the basin) were taken from twenty-five sampling sites under native vegetation (i.e., with no anthropogenic influence) at 0–20 cm depth in order to represent the diversity of soil classes and soil parent materials. These samples cover all sites under no or minimal anthropic influence. We ruled out some additional potential sampling sites due to evidence of anthropogenic influence and we would therefore like to emphasize the low occurrence of sites under fully preserved referenced conditions. On this basis, we feel that our sampling strategy was pragmatic.

(ii) the lithology of the catchment is provided, shown with perhaps too much detail (20 lithologies while only 25 soil samples!) in Figure 1, but not explained in terms of geological terranes, that is, whether and how close they are genetically related;

Response: We have completely revised the original Figure 1 – see new Figure 1 in the revised m/s with changes marked.

(iii) soil types (and respective percentage cover) are mentioned and two climatic zones are referred, but in both cases their likely geographical boundaries are not shown;

Response: Please see the new figure 1 in the revised m/s with changes marked.

(iv) granite samples are mentioned, but number, location of the actual sampling sites and the actual granite type are not referred nor shown in a map;

Response: Please see the new Figure 1 below and in the revised m/s with changes marked which now shows the location of the rock sampling sites and specifies the granitoid types in the legend.

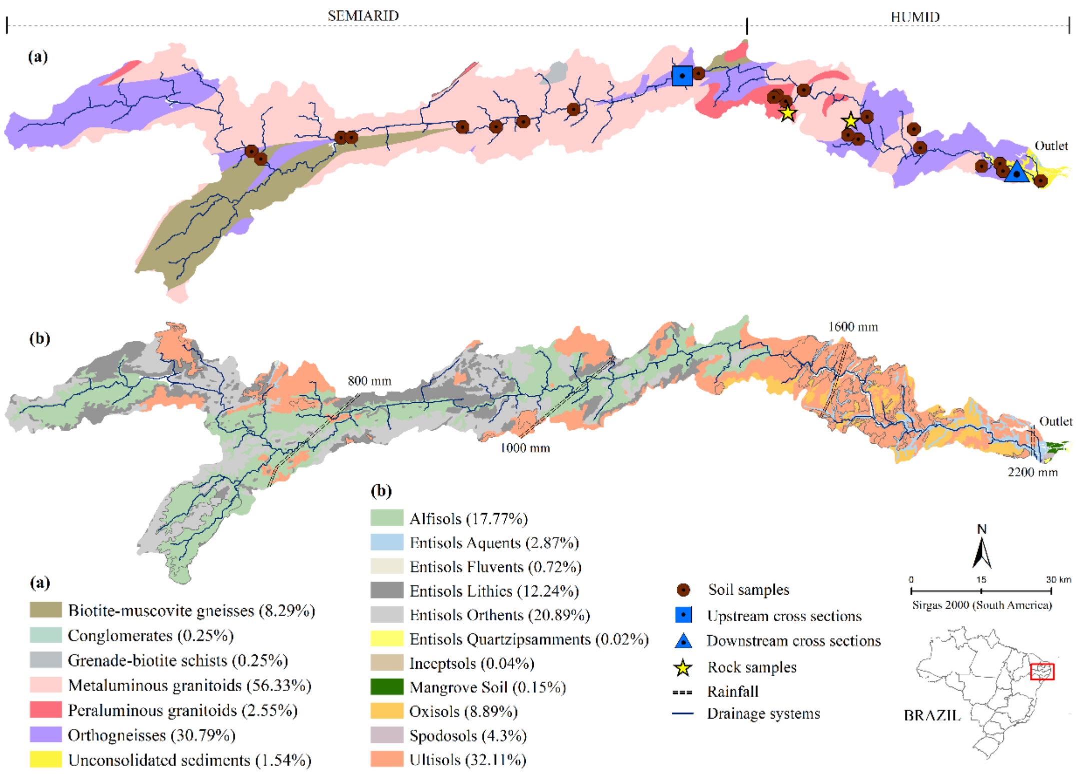

Fig. 1 Location of the Ipojuca catchment in Brazil, geology, soil classes and the distribution of soil and sediment sample collection points in the upstream and downstream sites.

In support of the revised Figure 1, new text is now found on ln 87-89 of the revised m/s with changes marked:

"Soil parent materials are mainly metaluminous granitoid (56%), orthogneiss (31%), and biotite-muscovite gneiss (8%) (Silva et al. 2015b) (Fig. 1). Soils in the catchment are predominantly Entisols (37%), Ultisols (32%), and Alfisols (18%)".

(v) the Th fluxes were determined in two cross sections for which the coordinates are given, but their actual location in a map is not shown;

Response: Please note that the locations have been added to the revised Figure 1 – see revised m/s with changes marked.

(vi) the soil samples are not listed in a table and the soil type, geology and climate are not assigned to each one of them; also, the other sampled materials (sediment, water and rock) are not adequately reported;

Response: Thank you for your suggestion. Please note that we added a soil map and climate information (demarcation of semi-arid and humid zones) n in the revised Figure 1 – see revised m/s with changes marked. In support of these changes, we added the following text on ln 85-87 of the revised m/s with changes marked:

"Average annual rainfall ranges from 600 mm in the semiarid, western region to 2400 mm in the coastal zone while annual average air temperature are 25 ºC and 28 ºC, respectively (Condepe/Fidem 2005)".

(vii) the analytical methods used, namely the samples' digestion, are questionable for the purpose, or at least, its use should be discussed in the manuscript, as the main thorium source is likely to be the resistate minerals, such as zircon, which hardly digest with the acid solution used; thus thorium concentrations and thorium specific activities are likely to be higher than the reported values;

Response: We understand the comment raised by the reviewer here. In fact, the method we deployed is not intended to accomplish total decomposition of the sample. In contrast, the method we used extracts the Th that is most likely to become available in the medium and long term (Alloway, 2013). This extraction is considered to represent the most environmentally relevant fraction (carbonates, sulphates, oxides and less labile phases) (USEPA, 1998; Löll et al. 2011). Thus, it does not extract the Th strongly bound to the silicate minerals. We therefore feel strongly that our method is applicable to determine Th in soils when one has an environmental concern as we do. Note that we are looking for background concentrations and quality reference values for future regulations on Th in soils. Most regulations do not consider total concentration (using HF), but, instead, environmentally available concentrations (using HCl and HNO_3). In addition, the German Soil Protection Regulation (BBodSchV, 1999) recommends extraction using aqua regia (HCl, HNO_3, 3:1) for estimating the "soil–human" exposure pathway.

On this basis, we edited the original text – see ln 124-127 in the revised m/s with changes marked:

'This method extracts the levels of Th that will probably become available in the medium and long term (Alloway 2013). In addition, the German Soil Protection Regulation (BBodSchV, 1999) and the Brazilian legislation (CONAMA, 2009) recommend extraction using HCl and HNO_3 (3:1) for estimating the "soil–human" exposure pathway'.

The full reference details for the Alloway (2013) citation are now provided in the revised m/s on ln 322-323. The full reference detials for the BBodSchV (1999) are now in the revised m/s with changes marked on ln 337-339. The detials for CONAMA (2009) are now included on ln 344-345.

(viii) the rationale for the list of elements and other parameters analysed together with Thorium (Th, Fe and Mn by ICP-OES after acid digestion, and "total" TiO2, Fe2O3, SrO and ZrO2 by XRF, plus LoI and pH) is not provided, and LoI is referred in materials and methods but not mentioned in the results and discussion;

Response: Please see below and in the revised m/s on ln 130-137 that we added the detection limits of elements determined in ICP and FRX. In addition, we also added into the revised m/s the variation of the loss on ignition data:

Calibration was carried out every ten samples and analysis was done only when the coefficient of determination (R^2) of the calibration curve was higher than 0.999. Whenever more than 10% deviation was observed, the equipment was recalibrated and samples reanalyzed. All analyses were performed in duplicate. Concentrations of Th, Fe, and Mn were determined by ICP-OES. The detection limits (mg kg^{-1}) were 0.01 for Th, 0.341 for Fe, and 0.005 for manganese. Recovery rates of the standard reference material were as follows (%): Th (94); Fe (93); Mn (85). Total TiO_2, Fe_2O_3, SrO and ZrO_2 concentrations were determined using XRF spectrometry (S8 TIGER ECO – WDXRF-1KW). Loss on ignition was determined at 1000 °C ranged from 1.1 to 4.7%. Detection limits (%) for TiO_2, Fe_2O_3, SrO, and ZrO_2 were 0.003, 0.1, 0.009, and 0.007, respectively.

(ix) the analytical results for soil, sediment and water samples are not shown in a table; the values reported in the caption of Figure 2 for the SEM-EDS granite samples should be shown in a table instead; and an adequate table of summary statistics for each sampled material should also be produced and shown;

Response: Thank you for your suggestion. We added a new Table 2 in the revised m/s with changes marked:

Table 2. Elemental composition of minerals in metaluminous and peraluminous granites in the Ipojuca watershed, Brazil, using a scanning electron microscope with energy-dispersive X-ray spectroscopy attached facilities (SEM-EDS)

Mineral	**Ce**	**P**	**La**	**Nd**	**Th**	**Pr**	**Sm**	**Si**	**Fe**	**Ca**	**Zr**	**U**	**Al**	**K**	**Ti**
Peraluminous granite (%)															
Monazite	34.0	17.0	16.0	11.0	10.0	4.0	3.0	2.0	1.5	1.5	-	-	-	-	-
Zircon	3.0	7.0	-	2.5	42.0	-	-	11.0	-	17.0	9.0	6.0	1.0	0.5	-
Metaluminous granite (%)															
Zircon	11.0	6.5	4.5	3.5	28.0	-	-	9.5	1.0	11.0	19.0	-	1.0	0.5	1.0

Additionally, please note below and in the manuscript that we added new text (ln 179-187) in support of the new Table 2:

‘Spatial variability of Th in soils (Fig. 2) showed a hotspot in lower middle regions of the watershed. Thorium concentrations in the hotspot at the downstream sites ranged from 24 to 72 mg kg^{-1}. Accordingly, this watershed area supplies a significant part of the total Th exported to the coastal zone. These hotspots are probably due to the abundance of monazite- and zircon-enriched granites (Figure 3a and 3b) with high Th concentration, i.e., 10% (Fig. 3a) and 28-42% (Table 2), respectively. Thorium is depleted in most rocks, but it can replace chemically closely related elements such as rare earth elements in some rocks (Taboada et al. 2006; Breiter et al. 2014; Kirkland et al. 2015). The downstream catchment sites are intensely weathered, but even recalcitrant minerals such as monazite and zircon might supply thorium. The low and high ZrO_2 concentration at upstream and downstream sites (Fig. 2) confirm this behaviour'.

(x) the method used for the production of the maps with the distribution and the probability of exceedance (not explained!!) of Th concentrations in soil are not explained and its use is, at least, highly questionable due to the linearity of the sampling sites;

Response: Yes, we agree with your observation here. We believe that the number of soil samples is not enough to show the distribution and the probability of exceedance. Thus, we deleted the original figure and added a new one in order to show the Th and Zr concentrations using the subdivision of Jenks natural breaks (five categories) – see revised Figure 2 in the revised m/s with changes marked:

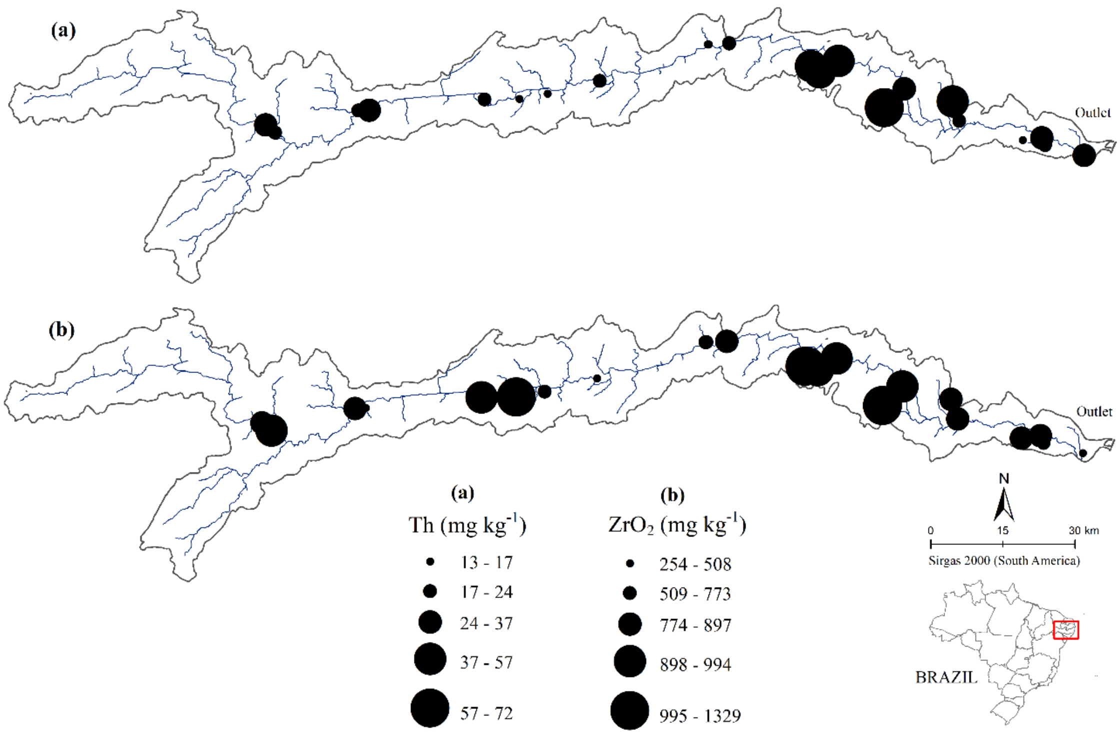

Fig. 2 Spatial distribution of the background concentrations of Th and ZrO_2 in the Ipojuca watershed in Brazil.

The following new text (ln 179-187) was added in support of the new Figure 2:

'Spatial variability of Th in soils (Fig. 2) showed a hotspot in lower middle regions of the watershed. Thorium concentrations in the hotspot at the downstream sites ranged from 24 to 72 mg kg^{-1}. Accordingly, this watershed area supplies a significant part of the total Th exported to the coastal zone. These hotspots are probably due to the abundance of monazite- and zircon-enriched granites (Figure 3a and 3b) with high Th concentration, i.e., 10% (Fig. 3a) and 28-42% (Table 2), respectively. Thorium is depleted in most rocks, but it can replace chemically closely related elements such as rare earth elements in some rocks (Taboada et al. 2006; Breiter et al. 2014; Kirkland et al. 2015). The downstream catchment sites are intensely weathered, but even recalcitrant minerals such as monazite and zircon might supply thorium. The low and high ZrO_2 concentration at upstream and downstream sites (Fig. 2) confirm this behaviour'.

(xi) the statistical analysis of the data is poor and using questionable methods. The concept of the probability of exceedance of the quality reference values is interesting and should be further explained an explored;

Response: Thank you for your suggestion. We decided to remove the kriging and to add the point distribution map of the concentrations of Th in the sampled locations, using the subdivision of Jenks natural breaks (five categories) – see revised Figure 2 in the revised m/s with changes marked.

(xii) the values from the present work are compared with data from many other works, which is good. However, it needs to be less random, with more focus on similar examples, namely granite type / mining areas in Brazil and any other parts of the globe (ex.: SW England, Sweden, Portugal, France, China, Africa, North America, etc..), tha have been analysed using similar lab methods and assuring that the statistic parameters being compared are the same (e.g.: the arithmetic mean, median and geometric mean are not the same, and should not be directly compared!);

Response: We edited the draft m/s and now we are only comparing Th concentrations among soils derived from granites and gneisses. In addition, we added the corresponding global average value (UNSCEAR 2000) – see revised Table 1; also we used a common statistical parameter for comparison (i.e. the mean).

Table 1 Average Th concentrations (mg kg^{-1}) in soils of the Ipojuca watershed compared to existing international soil data.

Countries	**Th content (mg kg^{-1})**
This study	28.5
Brazil (Savanna biome)[1]	12
France[2]	5.9
Indian[3]	6.9
Malaysia[4]	80
Spain[6]	17.7
Worldwide[7]	7.4

[1]Marques et al. (2004); [2]Aubert et al. (2004); [3]Braun et al. (2018); [4]Sanusi et al. (2017); [5]Taboada et al. (2006); [6]UNSCEAR (2000).

The following revised text discusses the new Table 1 – see ln 159-164 in the revised m/s with changes marked:

'The background concentrations of Th in soils ranged from 13.2 to 72.3 mg kg^{-1}, with an average of 28.6 mg kg^{-1}. Such values are higher than those reported for soils derived from granite (Aubert et al. 2004; Taboada et al. 2006) and gneiss (Marques et al. 2004; Braun et al. 2018) worldwide (Table 1). Moreover, Th concentrations in soils from the Ipojuca watershed were higher than the average concentrations reported for soils under coal exploration (9.9 mg kg^{-1}; Hussain et al. 2018) , impacted by uranium tailings (15.1 mg kg^{-1}; Yan and Luo 2014), and affected by mining operation (12.8 mg kg^{-1}; Momčilović et al. 2013)'.

(xiii) the discussion is also poor, with parametric statistics, such as the arithmetic mean and the Pearson correlation being abusively and inconsistently used, while the number of samples for each case is not shown in Table 2;

Response: Thank you for your suggestion. We have replaced Pearson with a Spearman correlation due to the lack of normal distributions. We also decided to remove the correlations referring to the hotspot area due to the insufficient number of soil samples. Please note that we added the number of observations and included the corresponding statistical results in the revised text on ln 241-245:

'Soils easternly located (n = 13) commonly exhibit Th enrichment with an increase in ZrO_2 (0.49) ($p<0.1$) and a decrease in SrO (-0.69) ($p<0.01$), respectively (Fig. 2), while soils in the western parts (n = 12) exhibited Th enrichment with increasing Fe_2O_3 (0.79) ($p<0.01$), TiO_2 (0.67) ($p<0.05$), Fe (0.83) ($p<0.01$), Mn (0.58) ($p <0.05$) and SrO (-0.74) ($p <0.01$) depletion. Similar behaviour has been reported previously (Du et al. 2012; Négrel et al. 2018; Hussain et al. 2018)'.

And on ln 262-268:

'The mean soil Th concentrations were higher than in sediment samples at both cross sections (Figure 4). This finding suggests that Th originated mainly from weathering processes Thorium concentration in suspended sediments was positively correlated with Fe at the upstream (0.62, $p<0.01$) and downstream (0.66, $p<0.05$) cross sections as well as with Mn at both the upstream (0.63, $p<0.05$) and downstream (0.79, $p<0.01$) sections. Furthermore, Th concentration in the bed sediment samples showed positive correlations with Fe (0.91) and Mn (0.66) at the downstream cross section, $p<0.01$ and $p<0.05$, respectively. Silva et al. (2015a) reported similar behaviour among Fe and various trace elements (Pb, Cr, Cu, Ni, Hg, As)'.

(xiv) The comparison of Th concentrations in soil and sediment loads is poor. It does not mention the differences in grainsize, and the (high) content in the study area of resistate thorium host minerals, such as zircon and monazite, is not adequately explored (for instance, using elements' ratios) aiming for a better understanding of the Th partition between soil and sediments;

Response: Thorium concentration in soils was higher than those observed for suspended sediments. We recognise this as a possible limitation of the study but it would be a problem if we had observed the highest Th concentrations in suspended sediments. In Brazil, a national regulation developed to establish QRVs in soils (CONAMA 2009) requires the use of < 2-mm fraction for soil. So, we understand that even if we compare the same grainsize, the concentration in soils would keep the highest one not changing our discussion. Please note that DH-48 sampler collects only silt and clay fractions and there is no remaning sample due to the difficulty linked to the suspended sediment sampling in rivers. We would have separated the silt and clay fraction in soil samples if we had observed the highest Th concentration in suspended sediments. We agree that this is an importante point but in our study it will not change the discussion. We strongly believe that soil will keep showing the highest concentration.

(xv) Despite of some good references reported, the introduction needs much more information about thorium, namely about its isotopes, sources, chemistry and behaviour

in the surface environment (namely in soil and water), and any biological interactions and exposure routes. Note that Th bio-geo-chemistry is quite different from that of Uranium and other elements more often included in environmental studies, such as, As, Cd, Cr, Cu, Pb, Sn, Zn, etc.. Also, its use by man is clearly not comparable yet. But i agree that assessing the natural background for Th or, at least, assessing its baselines, is a fundamental task. Man always impact the environment wherever they go or do... but in what extent the referred industrial complex (what do they do??), or the sugarcane, or the lack of sanitation, can turn thorium into an environmental concern? The levels of pollution allegedly reported for Pb and Zn in previous studies (in Introduction) cannot be simply implicitly 'extrapolated'
to Th.

Response: We thank the reviewer for recognising that greater understanding of Th context and fluxes is a current research gap for filling. To address the review comment here, the following paragraph was added to the revised m/s with changes marked on ln 52-56:

The following paragraph was added: “The primary anthropogenic Th sources are mining, milling, and processing operations. The use of phosphate fertilizers has also been one of the factors responsible for Th inputs into catchment soils and waters (Mazzilli et al. 2000; Salute and Mazzilli 2006; Conceição et al. 2009; Servitzoglou et al. 2018). Thorium has been used in small amounts as a replacement to uranium in nuclear reactor fuels (Xiao et al. 2016), which has increased Th environmental exposure”.

In addition, the following sentence was added on ln 67-71 of the revised m/s with changes marked

‘This catchment encompasses various potentially environmentally-threaten activities, including a port industrial complex (Suape) that ships over eleven million tons of chemical products and vast areas under sugarcane cultivation. Along with Suape complex, Ipojuca catchment surroundings have faced an industrial and urban development that puts additional pressure on the environment (Silva et al. 2015b)’.

The full reference details for Silva et al. (2015b) have been added to the revised reference list on ln 439-441.

The following original sentence was deleted: “The lack of urban sanitation in most municipalities along its watercourse is another cause of negative environmental impacts that requires monitoring”. “The lack of sanitation is not expected to be an important Th source”

The consistency of the background values and of the quality reference values is, thus, questionable, and the quality of the writing do not help overcoming this issue.
Given the issues raised above, I suggest the authors to address them as much as possible, namely:
(a) taking time in improving the Materials and Methods, with a clear structure and a clear focused text, thoroughly addressing sampling and analysis for each material (soil, bed and suspended sediment, water, granite samples), and clearly pointing out the related pros and cons of the materials and methods for the purpose; including an explanation about the list of elements and other parameters used;

Response: We have revised the Materials and Methods section – see edited text on ln 85-92, 104, 110, 115-117, 123-127, 130-137, 149 and 150-156.

(b) to adequately show the data and its stats in tables; rework the figures;
Response: We have revised Figures the original Figures 1 and 2 and the original Tables 1 and 2 – see revised m/s with cnanges marked.

(c) to attempt using auxiliary data, such as the geology / lithology, soil type, climatic zone (or meteorological data, if available), elevation (if easily available), human occupation, etc, to improve the interpolation of Thorium and its probability of exceedance across the area, aiming to overcome the problems mentioned above;

Response: We replaced the kriging in the original m/s with a new Figure 2:

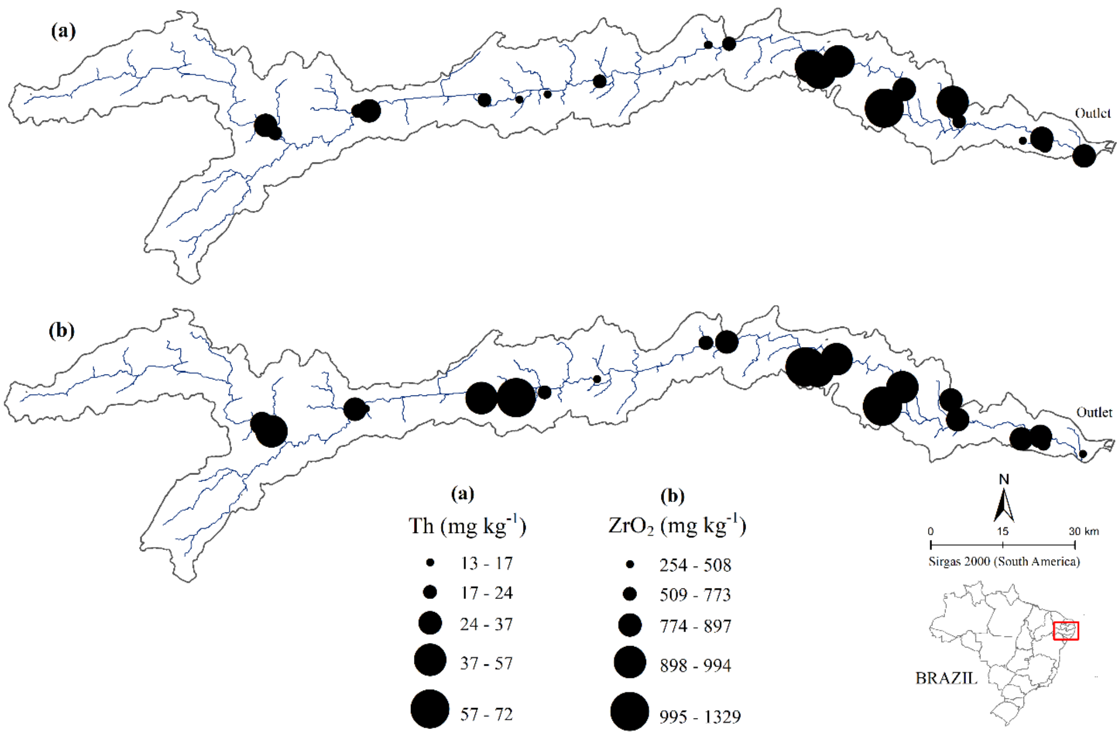

Fig. 2 Spatial distribution of the background concentrations of Th and ZrO_2 in the Ipojuca watershed in Brazil.

(d) to get informed about Compositional Data Analysis and its increasing use in environmental geochemistry, and to attempt using its principles, namely with the use of logratios and, perhaps, of multivariate techniques, aiming to improve the data analysis and the understanding of processes with thorium in the watershed under study; This will certainly allow to improve the discussion.

Response: We are grateful for the suggestion. We did not apply multivariate techniques such as principal component analysis or factor analysis because similar results were obtained using a simple correlation analysis. However, we agree that in some papers the main problem is the lack of recognition that the authors are dealing with compositional data and the biases this can create for correlations, FA and other statistical methods if

closure effects are not removed. We have followed a simple correction method such as additive log ratios (alr-) or centred log ratios (clr-) in other manuscripts of our team which are very easy to calculate as shown by:
Tolosana-Delgado R., 2008. Compositional Data Analysis in a Nutshell, www.sediment.unigoettingen.de/staff/tolosana/extra/CoDaNutshell.pdf

(e) the Dataset on its own may deserve to be published, but the authors need to show it very neatly, by clarifying the methods; adequately showing the study area, samples and results; improving the statistical analysis and better exploring the diversity of materials sampled and analysed; and bringing data limitations and advantages into the discussion;

Response: the above details throughout the response to review clarify how we have addressed these comments here.

(f) the text needs to be less vague, more focused and accurate, with a better scientific language in all its sections. I'm not sending suggestions on the PDF, as they would be too extensive.
Response: We have revised the text on ln 52-56, 67-71, 85-92, 104, 110, 115-117, 123-127, 130-137, 149, 150-156, 159-164, 171-245, 262-268.

We would like to thank the editor and anonymous reviewers for their insightful and constructive comments that greatly contributed to the improvement of the original manuscript.

Thorium content in soil, water and sediment samples and fluvial sediment-associated transport in a catchment system with a semiarid-coastal interface, Brazil

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Abstract

Thorium (Th) is one of the main sources of natural radiation to ecosystems. However, data regarding Th concentrations in rocks, soil, water and sediments are currently scarce. Accordingly, this study aimed to establish background concentrations and quality reference values (QRVs) for Th in the environmentally impacted Ipojuca River catchment in Brazil, where the weathering of granites releases Th into the environment. Additionally, the study aimed to calculate Th fluxes in water, and both bed and suspended sediment. The mean Th concentration in the study catchment soils was 28.6 mg kg^{-1}. The QRV for Th was estimated to be 21 mg kg^{-1} and 86.3 Bq kg^{-1}. Bed and suspended sediment-associated concentrations ranged from 2.8 to 32.9 mg kg^{-1}. Suspended sediment-associated discharge (3.42 t year^{-1}) accounted for more than 99% of the total Th flux, whilst the dissolved phase transport was negligible in comparison. At the downstream cross section in the study catchment, suspended sediment samples exhibited Th concentrations similiar to those observed in rivers impacted by mining activities. The discharge of sediment to the ocean from the study area is mainly triggred by soil erosion processes in the hotspot region (middle-inferior course). It is essential to identify Th hotspots before establishing environmental policies regarding human health and environmental protection.

Keywords: Quality reference values, Environmental quality, Watershed, Th hotspot, Sediment-associated transport, Soil erosion processes

Introduction

Thorium is a radioactive metal that is present in the environment in different species. ^{232}Th is the most abundant natural isotope (Holden 1990; Aggarwal 2016). High Th levels in the environment, derived from either natural or anthropogenic sources, increase exposure to other hazardous radioelements as a result of the corresponding decay series (Kritsananuwat et al. 2015; Danyłec et al. 2018). As a result, Th concentrations and the concomitant risks to ecosystems and human health have been investigated in various environmental settings around the world (Dragović et al. 2014; Sanusi et al. 2017; Bangotra et al. 2018; Cinelli et al. 2018; Négrel et al. 2018). Catchment scale assessments are, however, scarce. In Brazil, for example, existing studies have focused on partial evaluations of Th dynamics (Fernandes et al. 2006; Nascimento and Mozeto, 2008; Conceição et al. 2009; Guimarães et al. 2013; Ribeiro et al. 2017) and therefore do not assess the potential variability of Th in different environmental compartments including water and different types of fluvial sediment.

The primary anthropogenic Th sources are mining, milling, and processing operations. The use of phosphate fertilizers has also been one of the factors responsible for Th inputs into catchment soils and waters (Mazzilli et al. 2000; Saueia and Mazzilli 2006; Conceição et al. 2009; Servitzoglou et al. 2018). Thorium has been used in small amounts as a replacement to uranium in nuclear reactor fuels (Xiao et al. 2016), which has increased Th environmental exposure. In this context, an understanding of the natural background Th concentrations in soils is the first step to establishing soil screening levels for risk assessment and environmental policies for human health and environmental protection.

Sediments connect landscape units in a hydrographic basin (Wohl et al. 2018; Heckmann et al. 2018) and, consequently, sediment-associated transport can redistribute and tranfer Th through different ecosystems (Coynel et al. 2007; Rodrigues et al. 2018). In an exorreic drainage system, for example, sediment-associated redistribution transfers Th from soils to the fluvial network and from there to the ocean. In this scenario, Th concentrations in sediments reflect natural catchment sources and any additional inputs from anthropogenic activities.

The Ipojuca catchment has been highlighted as one of the most polluted in Brazil (Silva et al. 2015a, 2017). Here, high trace element fluxes in association with suspended sediments, especially Pb (28.2 t year^{-1}) and Zn (18.8 t year^{-1}), have been reported for downstream sampling sites (Silva et al. 2015a). This catchment encompasses various potentially environmentally-threaten activities, including a port industrial complex (Suape) that ships over eleven million tons of chemical products and vast areas under sugarcane cultivation. Along with Suape complex, Ipojuca catchment surroundings have faced an industrial and urban development that puts additional pressure on the environment (Silva et al. 2015b). Against this background, the study reported herein focussed on the Ipojuca River catchment and undertook work to address the following objectives: (i) to determine the background concentrations and establish Quality Reference Values (QRVs) for Th in catchment soils, and; (2) to determine the concentrations and fluxes of Th in water, bed and suspended sediments, relating these estimates to potential anthropic sources in the study area. The ultimate aim was for new data from this study to help establish the relationship between the mass concentration and the specific activity of Th in soils and fluxes in sediments within a representative continental-estuarine-coastal interface in the South Atlantic.

Material and methods

Study area

The study was carried out in the Ipojuca River catchment, which extends (08° 09′ 50″– 08° 40′ 20″ S and 34° 57′ 52″–37° 02′ 48″ W) from the western semiarid region to the coast of Pernambuco state, Brazil. Its total river length of 290 km drains a catchment area of ~3435 km^2 (CONDEPE/FIDEM 2005). The Ipojuca catchment includes the Industrial Harbor Complex of Suape and a large area under commercial sugarcane production. Moreover, the study basin includes about 24 municipalities, most of which have no sewage collection and treatment system (Lima Barros et al. 2013). Average annual rainfall ranges from 600 mm in the semiarid, western region to 2400 mm in the coastal zone while annual average air temperature are 25 ºC and 28 ºC, respectively (Condepe/Fidem 2005). Soil parent materials are mainly metaluminous granitoid (56%), orthogneiss (31%), and biotite-muscovite gneiss (8%) (Silva et al. 2015b) (Fig. 1). Soils in the catchment are predominantly Entisols (37%), Ultisols (32%), and Alfisols (18%).

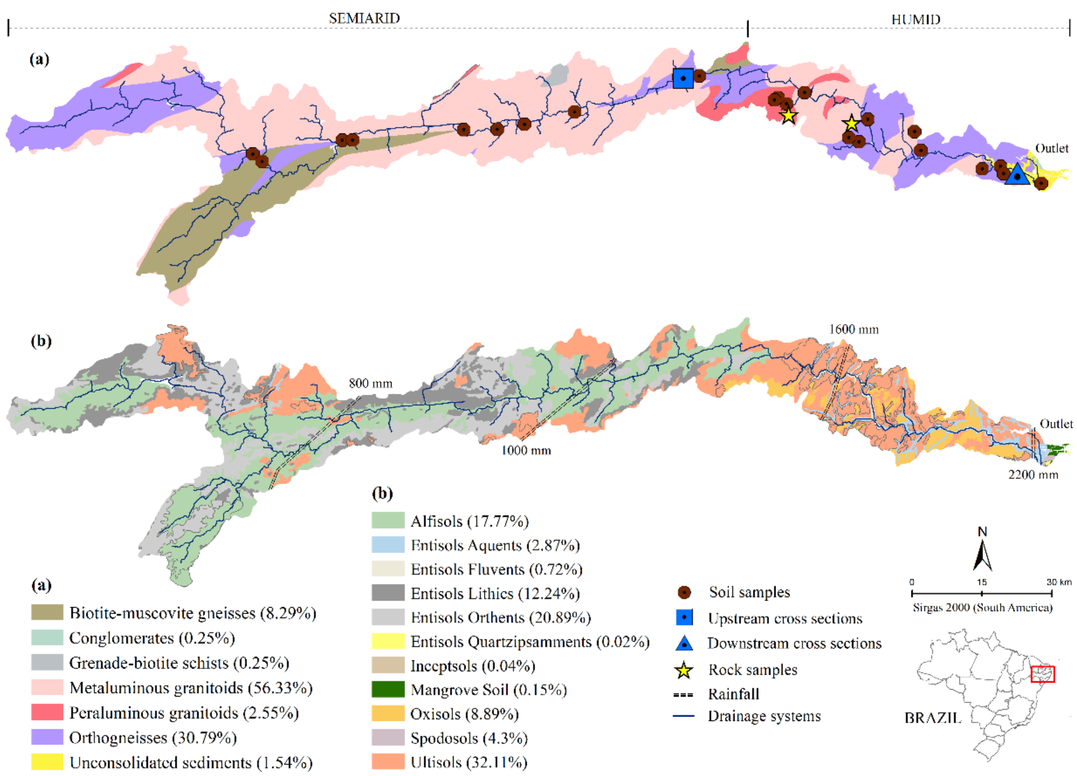

Fig. 1 Location of the Ipojuca catchment in Brazil, geology, soil classes and the distribution of soil and sediment sample collection points in the upstream and downstream sites.

Catchment sampling and laboratory analysis of rock, water, soil and sediments

Samples of granite, the most common rock type observed in the Ipojuca River catchment (Fig. 1) were collected and the mineralogical identification made from fine polished sections using a petrographic microscope (Murphy 1986). Here, granite samples were coated with a 20 nm gold layer (model Q150R - Quorum Technologie) for mineral identification using scanning electron microscopy (SEM; TESCAN, VEGA-3 LMU) at an accelerating voltage of 15 kV. Afterwards, an energy dispersive X-ray spectroscopy (EDS) detector (Oxford Instrument, model: 51-AD0007) coupled with SEM was used to determine the elemental composition of the mineralogical assembly that could act as a potential source of Th to the different environmental compartments of the study basin.

The background values for Th in soils collected from the study catchment were determined for reference sampling sites (i.e., areas under preserved native vegetation or with minimal anthropic influence). A total of 25 (12 in the semiarid region and 13 in the humid area) (Fig. 1) composite topsoil samples (i.e., uppermost 20 cm without the superficial organic layer and comprising, in total, 100 subsamples – four sub-samples per composite), were retrieved, to represent the diversity of soil classes and soil parent materials (Silva et al. 2015b). The composite soil samples were air dried, homogenized and dry-sieved through a 2 mm mesh.

Water, bed and suspended sediment samples were collected from both upstream (08° 13′ 10″ S – 35° 43′ 09″ W) and downstream (08° 24′ 16″ S – 35° 04′ 03″ W) cross sections (Fig. 1) under low and high water discharge regimes. Both cross-sections were sampled concurrently to ensure the same water flow conditions. The respective mean flow depths ranged from 0.27 to 0.56 m and 0.8 to 2.43 m, while the corresponding mean channel widths ranged from 6.0 to 10.80 m and 21.80 to 30.3 m, in the upstream and downstream cross sections, respectively. The depth-averaged velocity was obtained using an electromagnetic current meter adjusted in each vertical as a function of depth (USGS 2005). Suspended sediment samples were collected using a US DH–48 sampler. Twenty-four direct measurements (twelve in each cross section) were carried out following the equal-width-increment (EWI) method in order to obtain a representative set of samples (Edwards et al. 1999). This approach allowed for obtaining isokinetic sampling for water and suspended sediments. The bed sediments was sampled using a BLH-84 sampler in the same vertical segments used to collect the suspended sediment samples. Suspended sediment (SSQ) and bedload (BQ) discharge were calculated following Horowitz (2003) and Gray (2005), respectively.

Aliquots (0.5 g each) of the soil, bed and suspended sediment samples were gently ground and passed through a 0.3-mm mesh stainless steel sieve (ABNT no. 50). Samples were then digested in Teflon vessels (12 mL acid solution—HNO_3/HCl, 3:1) in a microwave oven (USEPA 1998). We applied the same to the 5-mL water samples digestion. This method extracts the Th concentration that may become available in the medium and long term (Alloway 2013). Both the German Soil Protection Regulation (BBodSchV, 1999) and the Brazilian legislation (CONAMA, 2009) recommend Th extraction using HCl and HNO_3 (3:1) for estimating the exposure pathway "soil–human". Standard operational and analytical data quality assurance procedures were followed, including the use of calibration curves, high purity acids, curve recalibration, analysis of reagent blanks, and standard reference materials (2709a SanJoaquin Soil and 2710a Montana I Soil; NIST 2002). Calibration was carried out every ten samples and analysis was done only when the coefficient of determination (R^2) of the calibration curve was higher than 0.999. Whenever more than 10% deviation was observed, the equipment was recalibrated and samples reanalyzed. All analyses were performed in duplicate. Concentrations of Th, Fe, and Mn were determined by ICP-OES. The detection limits (mg kg^{-1}) were 0.01 for Th, 0.341 for Fe, and 0.005 for manganese. Recovery rates of the standard reference material were as follows (%): Th (94); Fe (93); Mn (85). Total TiO_2, Fe_2O_3, SrO and ZrO_2 concentrations were determined using XRF spectrometry

(S8 TIGER ECO – WDXRF-1KW). Loss on ignition was determined at 1000 °C ranged from 1.1 to 4.7%. Detection limits (%) for TiO_2, Fe_2O_3, SrO, and ZrO_2 were 0.003, 0.1, 0.009, and 0.007, respectively. The soil pH was analyzed in H_2O (1:2.5 soil:solution ratio). The quality of the data was verified by analyzing the certified sample SRM 2709 (NIST 2002). The recovery rates of the major elements (%) decreased in the following order: Ti (101) > Fe (100) > Sr (97) > Zr (95).

Bed- and suspended sediment-associated Th fluxes

Th fluxes in association with suspended sediment transport were calculated following the approach proposed by Horowitz et al. (2001). The Th flux associated with bed sediment transport was obtained by multiplying the amount of bed sediment crossing the cross sections (Gray 2005) with the respective Th concentrations. To reduce the uncertainties related to the estimation of the Th fluxes in the different sediment compartments, water discharge and either bed or suspended sediment-associated Th concentrations were determined for simultaneous data pairings.

Data analysis

Descriptive statistics and Spearman correlation analysis were applied in this study. QRVs for Th were calculated as the 75^{th} percentile of the frequency distributions (CONAMA 2009). The specific Th activities were calculated using the conversion factor provided by the Central Laboratory of Radiological Protection of Poland (Malczewski et al. 2004), on the basis of the mass concentration of ^{232}Th, assuming this specie has a natural radioactive equilibrium and is an integral part of the elementary chemistry of Th. Therefore, the soil sample containing 0.24 mg kg^{-1} of Th have 1 Bq kg^{-1} of ^{232}Th. Aiming to observe Th and ZrO_2 hotspots, spatial distribution maps of background concentrations were prepared taking into account five categories for Th and Zr concentration.

Results and Discussion

Background concentrations and QRVs for Th in the study catchment soils

The background concentrations of Th in soils ranged from 13.2 to 72.3 mg kg^{-1}, with an average of 28.6 mg kg^{-1}. Such values are higher than those reported for soils derived from granite (Aubert et al. 2004; Taboada et al. 2006) and gneiss (Marques et al. 2004; Braun et al. 2018) worldwide (Table 1). Moreover, Th concentrations in soils from the Ipojuca watershed were higher than the average concentrations reported for soils under coal exploration (9.9 mg kg^{-1}; Hussain et al. 2018) , impacted by uranium tailings (15.1 mg kg^{-1}; Yan and Luo 2014), and affected by mining operation (12.8 mg kg^{-1}; Momčilović et al. 2013).

Table 1 Average Th concentrations (mg kg^{-1}) in soils of the Ipojuca watershed compared to existing international soil data.

Countries	Th (mg kg^{-1})
This study	28.5
Brazil (Savanna biome)[1]	12
France[2]	5.9
Indian[3]	6.9
Malaysia[4]	80
Spain[5]	17.7
Worldwide[6]	7.4

[1]Marques et al. (2004); [2]Aubert et al. (2004); [3]Braun et al. (2018); [4]Sanusi et al. (2017); [5]Taboada et al. (2006); [6]UNSCEAR (2000).

The QRVs for Th in soils of the Ipojuca watershed were 21 mg kg^{-1} for mass concentration and 86.3 Bq kg^{-1} for specific activity; Th specific activity was about three fold higher than the corresponding estimate value (30 Bq kg^{-1}) reported for worldwide soils (UNSCEAR, 2000) and similar to mining soils in Brazil (90.8 Bq kg^{-1}; Peixoto et al. 2016).

Spatial variability of Th in soils (Fig. 2) showed a hotspot in lower middle regions of the watershed. Thorium concentrations in the hotspot at the downstream sites ranged from 24 to 72 mg kg^{-1}. Accordingly, this watershed area supplies a significant part of the total Th exported to the coastal zone. These hotspots are probably due to the abundance of monazite- and zircon-enriched granites (Figure 3a and 3b) with high Th concentration, i.e., 10% (Fig. 3a) and 28-42% (Table 2), respectively. Thorium is depleted in most rocks, but it can replace chemically closely related elements such as rare earth elements in some rocks (Taboada et al. 2006; Breiter et al. 2014; Kirkland et al. 2015). The downstream catchment sites are intensely weathered, but even recalcitrant minerals such as monazite and zircon might supply thorium. The low and high ZrO_2 concentration at upstream and downstream sites (Fig. 2) confirm this behaviour.

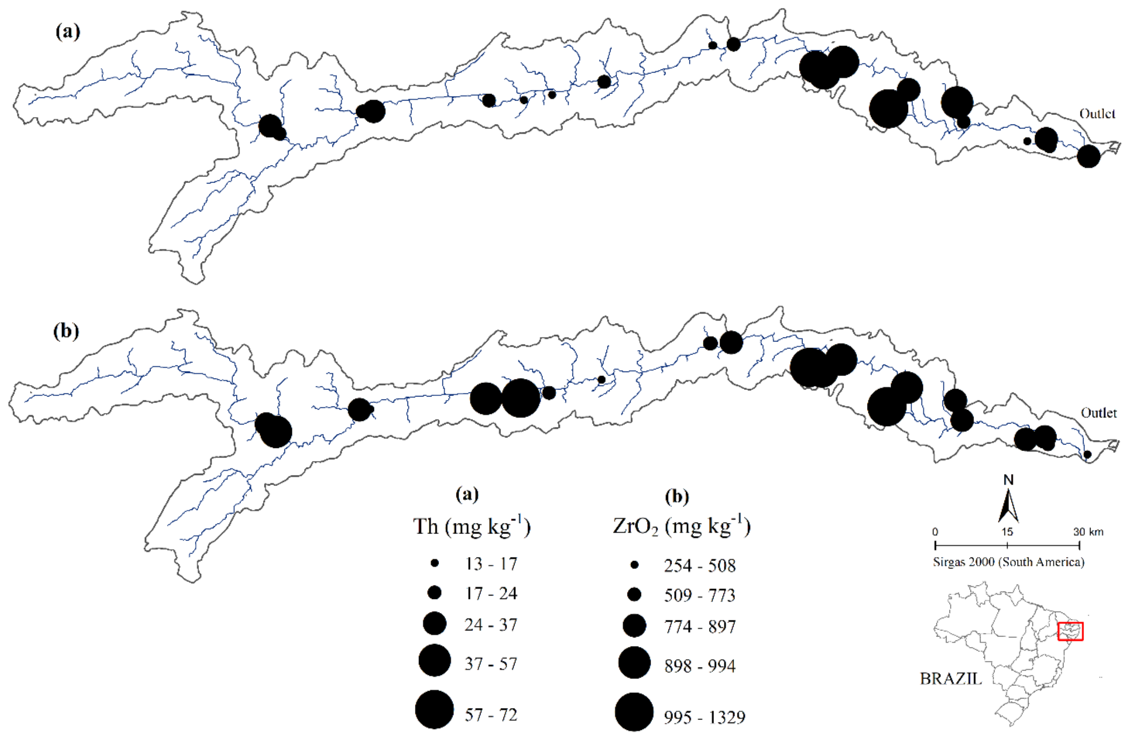

Fig. 2 Spatial distribution of the background concentrations of Th and ZrO_2 in the Ipojuca watershed in Brazil.

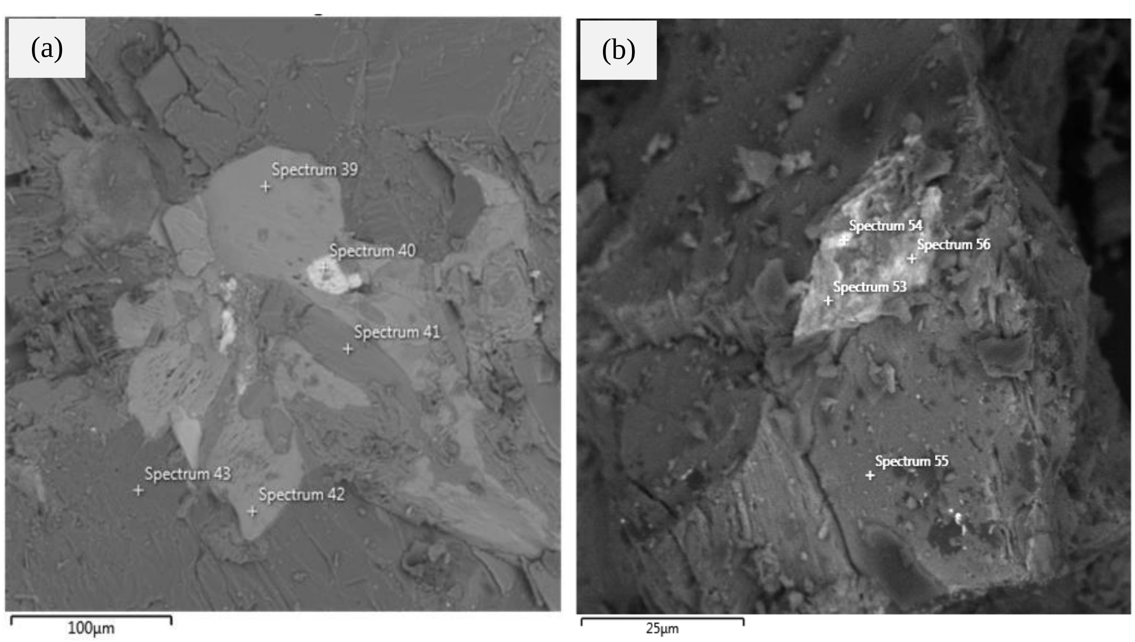

Fig. 3 Cross-section images of granites using a scanning electron microscope with energy-dispersive X-ray spectroscopy attached facilities (SEM-EDS) (a) Monazite (spectrum 40); zircon (spectrum 54) (b) Zircon (spectrum 56).

Table 2 Elemental composition of minerals in metaluminous and peraluminous granites in the Ipojuca watershed, Brazil, using a scanning electron microscope with energy-dispersive X-ray spectroscopy attached facilities (SEM-EDS)

Mineral	**Ce**	**P**	**La**	**Nd**	**Th**	**Pr**	**Sm**	**Si**	**Fe**	**Ca**	**Zr**	**U**	**Al**	**K**	**Ti**
Peraluminous granite (%)															
Monazite	34.0	17.0	16.0	11.0	10.0	4.0	3.0	2.0	1.5	1.5					
Zircon	3.0	7.0		2.5	42.0			11.0		17.0	9.0	6.0	1.0	0.5	
Metaluminous granite (%)															
Zircon	11.0	6.5	4.5	3.5	28.0			9.5	1.0	11.0	19.0		1.0	0.5	1.0

Soils easterly located (n = 13) commonly exhibit Th enrichment with an increase in ZrO_2 (0.49) ($p<0.1$) and a decrease in SrO (-0.69) ($p<0.01$), respectively (Fig. 2), while soils in the western parts (n = 12) exhibited Th enrichment with increasing Fe_2O_3 (0.79) ($p<0.01$), TiO_2 (0.67) ($p<0.05$), Fe (0.83) ($p<0.01$), Mn (0.58) ($p<0.05$) and SrO (-0.74) ($p<0.01$) depletion. Similar behaviour has been reported previously (Du et al. 2012; Négrel et al. 2018; Hussain et al. 2018).

Th concentrations in water and sediment samples

Sediment-associated Th concentrations exhibited the following order: suspended sediments at the downstream cross section (32.9 mg kg^{-1}) > bed sediments at the downstream cross section (15.8 mg kg^{-1}) > bed sediments at the upstream cross section (8 mg kg^{-1}) > suspended sediments at the upstream cross section (2.8 mg kg^{-1}) (Fig. 4). The mean Th concentration (14.9 mg kg^{-1}) in sediment samples was found to be similar to those reported for rivers in both India (7.5 mg kg^{-1}; Braun et al. 2018) and England (15 mg kg^{-1}; Ferreira et al. 2018). At the downstream cross section, suspended sediment samples showed Th concentrations similiar to those observed in rivers impacted by mining activities in Nigeria (28.7 mg kg^{-1}; Oyebamiji et al. 2018) and Portugal (32.6 mg kg^{-1}; Neiva et al. 2014), but lower than those values reported for the Diz (90.7 mg kg^{-1}; Antunes et al. 2018), and Mondego (185 mg kg^{-1}; Neiva et al. 2016) Rivers, in Portugal.

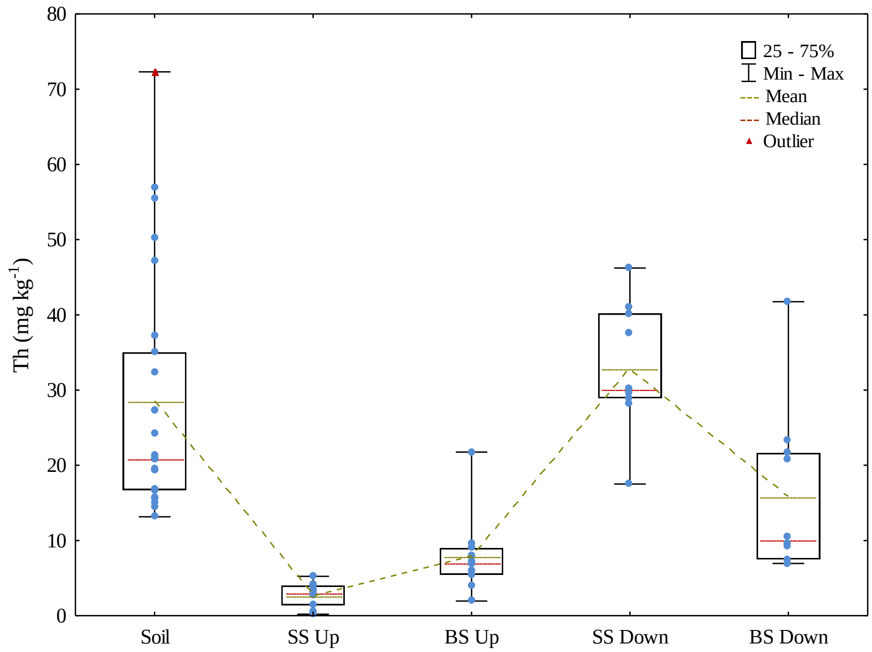

Fig. 4 Th concentrations (mg kg^{-1}) in the study catchment soils plus the bed and suspended sediment samples collected at both cross sections in the Ipojuca River. SS = suspended sediments; BS = bed sediments; Up = upstream cross section and Down = downstream cross section.

The mean soil Th concentrations were higher than in sediment samples at both cross sections (Figure 4). This finding suggests that Th originated mainly from weathering processes Thorium concentration in suspended sediments was positively correlated with Fe at the upstream (0.62, $p<0.01$) and downstream (0.66, $p<0.05$) cross sections as well as with Mn at both the upstream (0.63, $p<0.05$) and downstream (0.79, $p<0.01$) sections. Furthermore, Th concentration in the bed sediment samples showed positive correlations with Fe (0.91) and Mn (0.66) at the downstream cross section, $p<0.01$ and $p<0.05$, respectively. Silva et al. (2015a) reported similar behaviour among Fe and various trace elements (Pb, Cr, Cu, Ni, Hg, As).

The mean Th concentrations in water samples were consistently low: 0.007 mg L^{-1} and 0.005 mg L^{-1} at the upstream and downstream river cross sections, respectively. These values are 6 and 8 times lower than those values reported elsewhere for worldwide rivers (Gaillardet et al. 2003). The low concentrations in water was primarily due to the mean pH of 7.0. High Th concentrations in the sediment compartments of rivers is often reported under this pH (Coynel et al. 2007; Rodrigues et al. 2018).

Suspended and bed sediment-associated Th fluxes

Sediment-associated Th fluxes followed the order: suspended sediment-associated at the downstream cross section > suspended sediment-associated at the upstream cross section (6.6 x 10^{-2} t $year^{-1}$) > bed sediment-associated at the upstream cross section (9.5 x 10^{-4} t $year^{-1}$) > bed sediment-associated at the downstream cross section (6 x 10^{-4} t $year^{-1}$). The sediment-associated Th flux was thereby 50 times higher at the downstream river cross section. The major reasons were judged to be: (1) the hotspot located in the lower middle section of the study area as shown in Fig. 3, and; (2) potential different sediment characteristics at the two river cross section sites. A high positive correlation between Th and Fe in the suspended sediment samples suggested that Th is mainly being transported in association with sediment-associated oxyhydroxides to the coastal zone.

Suspended sediment accounted for more than 99% of the total Th flux, with the corresponding dissolved phase transport being negligle in comparison. Suspended sediment-associated Th fluxes at the downstream river cross section were estimated to be comparable to those observed for both trace elements (Cr – 2.92, Cu – 2.92, Ni – 1.53, As – 0.89, Cd – 0.018 and Hg 0.006 t year^{-1}; Silva et al., 2015a) and rare earth elements (La – 3.38 and Pr – 1.27 t year^{-1}; Silva et al. 2018) as well as those values observed for the largest European Subarctic River, the Severnaya Dvina River, located in Russia (3.64 t over five months; Pokrovsky et al. 2010). The transfer of sediment from exorreic river systems is one of the major Th transfer pathways to the world's oceans (Kienast et al. 2016). However, in the case of the Ipojuca River study catchment, this natural Th flux towards the ocean might not take place due to the construction of the Industrial and Harbour Complex of Suape which has changed natural hydrological and morphological conditions. For instance, Muniz et al. (2005) observed that the antropic obstruction of the fluvial system triggered enhanced suspended sediment sedimentation. As a result, the water flow depth has decreased. Therefore, the Atlantic Ocean might not be the final receptor of the suspended sediment-associated Th fluxes from the Ipojuca River catchment wich, in turn, highlights the importance of understanding impacts on the intermediate estuarine transitional environments.

Conclusion

There is no evidence of anthropogenic impacts on Th concentrations in water and sediment samples collected in the Ipojuca River catchment based on the comparison of the background levels and QRVs (21 mg kg^{-1} and 86.3 Bq kg^{-1}). Thorium supply is mainly governed by soils derived from granites, containing high proportions of monazite and zircon. High Th background concentrations were observed in the local soils, with revealing a hotspot area in the lower middle portions of of the study area. The hotspot highlights the importance of discussing the representativeness of QRVs for either local or regional conditions.

Suspended sediment accounted for more than 99% of the total Th flux from the study catchment. At the downstream cross section, suspended sediment samples exhibited Th concentrations similiar to those observed in rivers impacted by mining activities. The amount of sediment supplied to the ocean is mainly triggered by catchment soil erosion and sediment mobilisation processes and it is therefore essential to identify these critical sources of sediment dleivered to the river channel system to support designing and establishing environmental policies for protecting human and environmental health.

Acknowledgements

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