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Validation of a database of mean uranium, thorium and potassium concentrations in rock samples of Portuguese geological units, generated of literature data

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Highlights

- A database of U, Th and K concentrations in rocks of Portugal established;

- Mean U, Th and K concentrations in rock per geological unit calculated;

- Validation by comparison of calculated to measured mean terrestrial dose rate;

- Investigation of variance components traceable to the geochemical analysis;

- Use of scattered local geochemical data to establish large scale maps enabled.

1   **Abstract**

2   The European Atlas of Natural Radiation has been under development for the past

3   15 years. Among the lacunae of the Atlas are maps of U, Th and K concentrations in

4   rocks due to lack of European-wide geochemical surveys of bedrock units. The objective

5   of this paper is to investigate the usability of scattered geochemical data of rock samples

6   for large-scale mapping of U, Th and K concentrations in geological units. For this

7   purpose, geochemical data were compiled from grey literature sources to produce a

8   geochemical database (LIT database) that includes 2817 results of U, Th and K

9   concentrations measured in rock samples.

10   Given the methodical heterogeneity within LIT database, the influence of the

11   geochemical analysis techniques was assessed through a three-way analysis of

12   variance (ANOVA) using geological units, geochemical analysis techniques and loss on

13   ignition (LOI) as categorical variables. The percentage of variation explained by

14   geological factors was 53 % for U, 38 % for Th, 50% for K and 51 % for the terrestrial

15   gamma dose rate (TGDR), while the percentage of variation explained by the

16   geochemical analysis techniques and LOI was generally lower than 5 %. The geological

17   factors were thereby the main source of variability in the data, followed by the error

18   component which can be assumed to represent true spatial variability of geochemical

19   concentrations, hence, variability within the geological units. The reliability of LIT

20   database between the different geochemical analysis techniques was investigated

21   through pairwise comparison of the least square (LS) means computed through the

22   three-way ANOVA for each geochemical analysis technique. The results show an

23   agreement of the LS means between the different geochemical analysis techniques,

24   which indicates that LIT database can be considered consistent within itself, thus,

25   reliable.

26   In order to validate the usability of literature data, the TGDR calculated from literature

27   data ($TGDR_{calc}$) was compared to the measured TGDR ($TGDR_{obs}$) displayed in the

28   Radiometric Map of Portugal (RMP) using geological units as reference units. The

29   correlation between $TGDR_{calc}$ and $TGDR_{obs}$ was highly significant ($p < 0.001$) and the

30   results of a paired sample t-test and Wilcoxon median tests indicate that the differences

31   between the arithmetic means of $TGDR_{calc}$ and $TGDR_{obs}$ were not statistically significant

32   ($p = 0.126$ and $p = 0.14$, respectively). Distributions of $TGDR_{calc}$ and $TGDR_{obs}$ are

33   seemingly equal according to the Kolmogorov-Smirnov and Anderson-Darling tests. The

34   pooled standard deviation (SD) of the RMP dataset was set as criterion to assess the

35   discrepancy between the arithmetic means of the RMP and LIT databases. About 14 out

36   of 26 geological units are located within one pooled SD around $TGDR_{obs}$ and only 1 out

37   of 26 units is located outside 2 pooled SDs. Systematic discrepancies were observed for

38   sedimentary rocks possibly due to the lack of representativeness of the data.

39   Nonetheless, the compatibility of the RMP and LIT databases can be considered

40   acceptable, which implies that the estimation of the contents of terrestrial radionuclides

41   using literature data for large-scale mapping of U, Th and K contents in geological units

42   is reasonable.

45   **1. Introduction**

46   **1.1 Motivation**

47   A long-term European project, under way for about 15 years, is the European Atlas

48   of Natural Radiation, of which web and printed versions exist (Cinelli et al., 2019; EC,

49   2019). The Atlas is however incomplete, as certain compartments and environmental

50   media are missing or fragmentary due to lack of data. Among these lacunae are maps

51   of concentrations of naturally occurring radionuclides, namely isotopes of U, Th and K,

52   in rock. While Europe-wide geochemical surveys of *agricultural and pasture soil* including

53   these radionuclides exist (FOREGS and GEMAS, maps and references in the Atlas),

54   literature data of U, Th and K in *rock* are scattered and methodically highly

                                                                                          4

heterogeneous. Therefore, creating Europe-wide maps from such data appeared questionable. The alternative, on the other hand, namely creating a methodically homogeneous geochemical database of European rocks from scratch, would pose a tremendous task which is beyond realistic feasibility. Therefore, it has been concluded by the board of experts of the Atlas (to which the authors of this paper belong) to explore the feasibility of maps of U, Th and K concentrations in rocks, derived from literature data. This requires, as very first step, to investigate whether literature data can be used to this end, observing standards of accuracy and precision, given methodical heterogeneity. The objective of this paper is thus, investigating the usability of scattered geochemical literature data for large-scale (in perspective, European scale) mapping. As test region for this study we use the territory of Portugal and as geochemical data sources, local studies on rock geochemistry performed in Portugal.

1.2 Geochemical surveys

Local surveys of geochemistry are profusely available in scientific literature. Large scale surveys are, however, scarce because the generation of a truly representative sample of the media is difficult with limited resources, and sampling of the entire population of landscape units is impractical and costly.

UNESCO initiated the first attempt to create a geochemical map of the world in 1988 through the International Geochemical Mapping Project (IGCP 259) (Xuejing and Hangxin, 2001). The main goal of the project was to estimate the concentration of several elements at a global scale with particular focus on ore pathfinders and radioelements (Darnley 1995, Darnley et al. 1995, Xuejing and Hangxin, 2001). The project intended to overcome the lack of numerical equivalence between compiled datasets that are subject to different sampling and analytical techniques as well as different levels of quality control (Darnley et al. 1995). However, the compilation and normalization of existing datasets required that data at multiple spatial scales be interlinked (Darnley 1995, Darnley et al. 1995).

82   A compilation of geochemical data hardly fulfills the assumptions of statistical

83   inference (ex. the sampling must be random, unbiased and designed to adequately

84   represent the population, Crumbling, 2001; Ramsey and Hewitt, 2005) as the data have

85   been acquired for different purposes, at different scales and with different methods.

86   However, every geochemical survey must rely on a suitable knowledge of the geology

87   of the surveyed area (e.g. Rollinson, 1993). Thus, geochemical surveys can be

88   presumed to be representative of the geological units sampled.

89   The estimation of the contents of terrestrial radionuclides, radon, gamma dose rate

90   and air-absorbed dose rate using geochemical data has been attempted at both a local

91   (e.g. Ielsch et al. 2010; Ye and Gan, 2013) and regional scale (e.g. Appleton et al. 2008;

92   Beamish 2014; Ielsch et al. 2017; Marsac et al. 2016). However, the authors often resort

93   to geochemical data available in national databases that have been acquired with

94   consistent analytical techniques and quality control procedures.

95   **1.3 Heterogeneity of literature data**

96   Heterogeneity of literature data occurs on several levels. (1) The data come from

97   regional or local studies of certain rock formations or types with certain geochemical

98   objectives, such as mineral exploration, hydrological investigations etc. While

99   representativeness for the study area can be assumed, it is unclear to which extent this

100   applies to an entire lithological class.

101   (2) Sampling and sample geo-referencing methods are heterogeneous. For example,

102   many literature sources do not quote locations of individual samples, but only regions of

103   origin. Sometimes, no individual but only aggregated results are given, e.g. arithmetic

104   mean concentrations and standard deviations. This circumstance inhibits the use of

105   geostatistical tools.

106   (3) Finally, geochemical analytic methodology is heterogeneous. Comparability of

107   results between different studies is therefore not given a priori. Both radiological and

108   geochemical data can be used to evaluate U, Th and K concentrations and distributions

109   (IAEA, 2010). Radiological data refers to radionuclide concentrations determined

110   through alpha- or gamma-spectrometry while geochemical data may be acquired

111   through various geochemical analysis techniques (hereafter referred to as analytical

112   techniques), such as X-Ray Fluorescence (XRF), Induced Coupled Plasma

113   Spectrometry (ICP) or Instrumental Neutron Activation Analysis (INAA), among others.

114   It should be stressed again that heterogeneity between studies does not mean to

115   invalidate the individual studies, but it is an obstacle to using them as input for maps

116   beyond the scale of the individual ones. Investigating whether it is still possible, is the

117   subject of this paper.

118   **1.4 Variability of true and measured geochemical concentrations**

119   The idea underlying the analysis performed in this study is that there are essentially

120   three components of variability:

121   (A) Variability between geological units, leading to variance between geochemical

122   concentrations of samples (or studies, representing aggregated samples) located in

123   different geological units, as this factor is assumed to control geochemical concentration;

124   this component represents *true spatial variability* of the investigated variable

125   (geochemical concentration).

126   (B) Variance due to different analytical techniques, as it is known that different

127   techniques applied to the same sample, i.e. same true concentration, can lead to

128   systematically different results (e.g. Rollinson, 1993). This component refers to the

129   *observation process* of the variable, not to its true variability over a geological unit.

130   (C) Variance due to lack of spatial representativeness: assume two studies using

131   same analytical technique, performed in different parts of the same geological unit. Due

132   to true spatial variability within geological units, the results will still be different, in general,

133   in spite of variance sources (1) and (2) excluded. This effect can only be avoided

134   (asymptotically with sample size) if the sample covers the domain (geological unit)

135   representatively. (Representativeness means that the statistical distribution of the

136   sample is asymptotically the same as the true distribution of the investigated variable,

7

137 here geochemical concentration.) This component refers to availability of data within a

138 geological unit and their aggregation within and can be understood as sampling effect

139 induced by true variability, component (1). Getting hold of this component is particularly

140 difficult.

141 **1.5 Validation of usability of literature data**

142 The tool to validate the usability of geochemical literature data is comparison of

143 terrestrial gamma dose rate (TGDR) calculated from geochemical concentrations with

144 measured ones. Coincidence within tolerable deviation is a *necessary condition* of the

145 validity of regional estimates from scattered literature data. The strategy is therefore, 1)

146 estimate mean U, Th, K concentrations of geological units from literature data; 2)

147 calculate the mean TGDR per unit and 3) compare these calculated with measured mean

148 TGDR of the same units. This is possible for Portugal as test region, as a fine-grained

149 TGDR map of Portugal is available. If it is proven that creating maps of rock geochemistry

150 from scattered literature data is possible in Portugal, it can plausibly be assumed that

151 this is possible also in other regions.

152 **1.6 Organization of this paper**

153 In the methods section (2), we first establish the geological classification scheme

154 which leads to the set of geological units in which geochemical literature data are

155 aggregated and mean dose rates are calculated. This is followed by a presentation of

156 the compiled geochemical database (section 2.2) and the TGDR map of Portugal (2.3).

157 In section 2.4, the conversion of geochemical concentration into TGDR is reviewed and

158 in 2.5, we explain statistical techniques.

159 The results section (3) is firstly devoted to analyzing the sources of variance A and B

160 (geology and analytical techniques) in section 3.1. Then an attempt is made to remove

161 source B, to assess the effect of lack of representativeness at least qualitatively (section

162 3.2). The validation analysis through terrestrial dose rate is shown in section 3.3.

163 **2. Materials and Methods**

8

2.1. Geological classification scheme

OneGeology-Europe (OGE) data were chosen as the geological map to be used as reference because they are available at the European level (at http://www.onegeology-europe.org/), providing access to geological maps at the scale of 1:1,000,000 (Baker and Jackson, 2010). The OGE map for Portugal was developed through collaboration with the Portuguese National Laboratory of Energy and Geology (LNEG), and comprises three distinct layers, namely lithology, age and geological structures. The code classification scheme of the OGE map is equivalent to the code classification scheme of the Portuguese Geological Map (PGM) at the scale of 1:1,000,000 published in 2010 by LNEG, and available at http://geoportal.lneg.pt/geoportal/mapas/index.html. The OGE classification comprises 76 geological units in mainland Portugal and 11 units in the Madeira and Azores archipelagos. A summary description of the geological units studied in the present work is presented in Table 1 according to Baker and Jackson (2010). A simplified geological map is presented in Figure 1a.

2.2. The Radiometric Map of Portugal

The Radiometric Map of Portugal (RMP, Figure 1b, Batista et al. 2013) displays the terrestrial gamma dose rate in mainland Portugal and is further denoted as $TGDR_{obs}$. A raster layer is available freely at http://geoportal.lneg.pt/geoportal/mapas/index.html. The data were acquired with hand-carried, vehicle-borne and air-borne equipment from 1955 onwards (Batista et al. 2012). The equipment used were calibrated either using sources of terrestrial radionuclides with known concentrations of U, Th and K or by measuring the same sites with different equipment (Batista et al. 2012; Grasty et al. 1993). The first radiometric maps of Portugal were produced based on 733,201 measurement points by linear interpolation with the minimum curvature method. The estimation grid consists of 250 m $\times$ 250 m cells. A minimum of 10 measurement points was defined necessary for estimation on each grid point, to assure reasonable statistical reliability. This required a search radius of 10 km around every grid point to make sure that the required minimum

191 number of observations could be achieved (Torres et al. 1997; Saraiva et al. 1998). The

192 updated RMP was produced based on 841,440 measurement points following the

193 acquisition of new data to fill the gaps in the previously developed maps (Batista et al.

194 2012; Batista et al. 2013).

195 The cell size of the RMP constitutes an important limitation for geological units that

196 have a large perimeter to area ratio, such as vein-type rocks (perimeter to area ratio

197 generally higher than 5). The width of the f1 and f2 (basic vein-type rocks) and qz (quartz

198 veins) units is generally lower than 500 m. Given the RMP cell size of 250 m and the

199 search radius of 10 km used to reach a minimum of 10 measurement points for

200 interpolation, the $TGDR_{obs}$ for these units is highly influenced by the $TGDR_{obs}$ of

201 neighboring geological units. Therefore, the $TGDR_{obs}$ of vein-type rocks displayed in the

202 RMP is unreliable. For this reason, vein-type geological units were excluded from the

203 analysis. This is unfortunate because these units often contain concentrations of

204 radioactive elements strongly different from their surroundings and should therefore be

205 given particular attention for radioprotection reasons. The methical alternative would

206 have been a different interpolation scheme for such units, but the original raw TGDR

207 data which would be necessary for this, are not available to us.

208 The lack of access to the original raw TGDR data inhibits the assessment of the

209 influence of the presence of unconsolidated overburden and soil units in the measured

210 TGDR. However, the RMP was primarily developed for the purpose of mineral

211 exploration (Batista et al. 2012; Grasty et al. 1993, Saraiva et al. 1998; Tauchid and

212 Grasty, 2002; Torres and Grasty, 1993). Sampling was focused on the main geological

213 units, as surveys were carried preferentially over crystalline areas, followed by the

214 Mesozoic and Cenozoic sedimentary basins (Torres and Grasty, 1993). Data from car,

215 foot and air-borne surveys were calibrated through measurement of selected areas of

216 exposed bedrock of the main geological units (Torres and Grasty, 1993). The RMP thus

217 reflects the geological character of Portugal (Batista et al. 2012; Grasty et al. 1993,

218   Saraiva et al. 1998; Tauchid and Grasty, 2002; Torres and Grasty, 1993). Thus, the RMP

219   data can be presumed to be representative of the geological units.

220 **Table 1.** Summary description of the geological units studied according to OGE data

221 (Baker and Johnson, 2010).

Group	OGE unit	Perimeter/Area ratio	Lower age	Upper age	Predominant Lithology	Subordinate lithology
Sedimentary rocks	N2	0.9	Pliocene	Pliocene	Sandstone	Conglomerate, Siltstone
	N1c	1.2	Miocene	Miocene	Sandstone	Conglomerate, Siltstone
	K1-2	1.4	Cretaceous	Cretaceous	Limestone	Sandstone, Impure carbonate sedimentary rock, Dolomite
	K1	1.8	Early/Lower Cretaceous	Early/Lower Cretaceous	Sandstone	Limestone, Impure carbonate sedimentary rock, Dolomite
	TJ1	2.2	Late/Upper Triassic	Middle Jurassic	Sandstone	Claystone, Evaporite, Limestone
	C2	3.6	Pennsylvanian	Pennsylvanian	Conglomerate	Sandstone, Claystone, Coal
Metamorphic rocks	C1-2	0.3	Carboniferous	Carboniferous	Phyllite	-
	D2-3	1.9	Middle Devonian	Late/Upper Devonian	Phyllite	Quartzite
	SDof	1.2	Silurian	Devonian	Amphibolite	Schist, Fine grained igneous rock
	SD	0.4	Silurian	Early/Lower Devonian	Phyllite	-
	SDP	0.7	Ordovician	Devonian	Phyllite	-
	ODP	0.8	Ordovician	Devonian	Quartzite	-
	O_a	1.6	Ordovician	Ordovician	Quartzite	Phyllite
	gz	1.1	Furongian	Middle Ordovician	Orthogneiss	Granite, Diorite
	Npep	0.6	Ediacarian	Cambrian	Phyllite	-
	NP2	1.4	Neoproterozoic	Neoproterozoic	Phyllite	-
	NP1	1.6	Neoproterozoic	Neoproterozoic	Schist	Gneiss, Migmatite
Igneous rocks	GAMA2	3.8	Late/Upper Cretaceous	Late/Upper Cretaceous	Diorite	Gabbro
	CVL	2.2	Late/Upper Cretaceous	Late/Upper Cretaceous	Basalt	Pyroclastic material, Gabbro,
	g1_b	1.1	Pennsylvanian	Cisuralian	Granite	-
	g2_b	0.3	Pennsylvanian	Cisuralian	Granite	-
	g3	0.7	Pennsylvanian	Cisuralian	Granite	-
	g1_a	0.7	Mississippian	Pennsylvanian	Granite	-
	g2_a	0.7	Mississippian	Pennsylvanian	Granite	-
	g1a	0.8	Late/Upper Devonian	Pennsylvanian	Tonalite	Granodiorite,
	GAMA	1.3	Late/Upper Devonian	Pennsylvanian	Gabbro	Anorthositic rock, Diorite
	D3C1	1.4	Late/Upper Devonian	Pennsylvanian	Fine grained igneous rock	Phyllite

*The perimeter to area ratio was computed as the ratio between the sum of the perimeter to the sum of the area of all polygons of the geological unit.

222
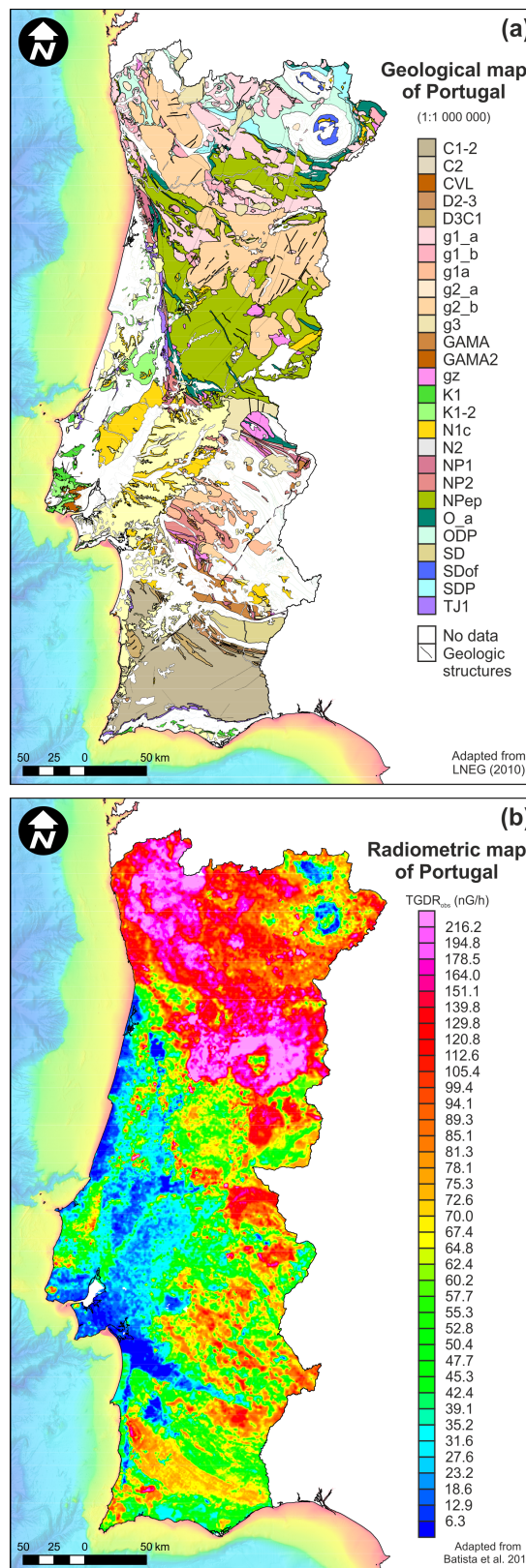
Figure 1. a) Geological units studied. Adapted from the Geological Map of Portugal at the scale of 1:1,000,000 (LNEG, 2010). **b)** Radiometric Map of Portugal (Batista et al. 2013). Bathymetry was retrieved from http://portal.emodnet-bathymetry.eu/mean-depth-full-coverage (last accessed in February 2017).

2.3. The geochemical database

A compilation of geochemical surveys available in mainland Portugal was carried out in order to produce a new geochemical database, called LIT to denote that is consists of literature data. The LIT database includes 2817 observations of U, Th and/or K concentrations measured in rock samples presumed to be representative of the geological units studied. The data included in LIT database were retrieved from the references listed in table A1 (Supplementary material). All samples included in LIT database were collected in areas of bedrock exposed on the earth surface excluding data retrieved from Cerejo (2013), Pinto (2014), Oliveira (2015) and Dinis et al. (2011) whom also studied rock samples retrieved from boreholes and/or underground galleries. Due to the inherent modifications caused by in-situ chemical and physical weathering, erosion and transport, among others, soil samples and unconsolidated materials are not considered representative of geological units, hence, were excluded from the analysis. Data for the Azores and Madeira archipelagos were not included in the database as the RMP only covers mainland Portugal (Batista et al. 2013).

Three types of samples were considered as observations: (1) individual analyses of rock samples; (2) analyses of composite samples (mixtures of several individual samples taken within an area, analyzed as one sample; the purpose is to reduce variability) and (3) averages of individual samples' analyses. Statistically, sample averages were treated as individual samples; (3) can be thought as mathematical mixing in analogy to physical mixing in (2). The accurate location of the sampling sites of the observations are mostly unknown inhibiting the use of geostatistical tools. This is because in earlier surveys, geo-referencing was not considered necessary. Due to this limitation, the regionalization of the available data was carried out using geological information.

Each observation of the LIT database was classified with a code of the geological classification scheme described in section 2.1. according to the location of the observations or the study area (when provided by the authors), or, in alternative, through

254 the lithologic, petrographic or paleontological features of the samples. A summary of the

255 data available by geological unit (Table A1) and by analytical techniques (Table A2) are

256 given as supplementary material.

257   For each observation of U, Th and/or K, the element concentration and analytical

258 techniques were registered as provided by the authors. No corrections to U, Th and/or K

259 concentrations were applied for loss on ignition (LOI) or the volatile content. A binary

260 categorical variable for the computation of the effects of LOI in an Analysis of Variance

261 (ANOVA) was defined. Each observation was classified as "TRUE" if the authors

262 estimated LOI (and/or the volatile content) but did not correct the data for LOI and

263 "FALSE" if the authors estimated and corrected the concentration of terrestrial

264 radionuclides using LOI data.

265   Values reported as below the lower limit of detection (LLD) as well as zeroes were

266 set to 0.65LLD or to an arbitrary small value in case the LLD was not provided by the

267 authors. The overall percentage of values below the LLD was 6% for U, 4% for Th and

268 less than 1% for K.

269 **2.4 Calculation of terrestrial gamma dose rate TGDR**

270   U, Th and K concentration were converted into activity concentration using

271 appropriate conversion factors (Table 2). The TGDR, further denoted as TGDR$_{calc}$, was

272 computed from U, Th and K activity concentration (in Bq/kg) according to the following

273 equation:

274 $$TGDR_{calc} = 0.0417 \times {}^{40}K + 0.462 \times {}^{238}U + 0.604 \times {}^{232}Th \qquad (1)$$

275   The dose conversion factors (in Bq/kg) of 0.0417, 0.462 and 0.604 were from

276 UNSCEAR (2010). All observations were considered valid, regardless of the analytical

277 technique used in the analysis, and representative of the geological unit sampled by the

278 authors. The database of U, Th and K contents in activity concentration is presented as

279 Supplementary material (Table B1).

Table 2. Conversion factors.

From	To	Conversion
U (mg/kg)	^{238}U (Bq/kg)	^{238}U (Bq/kg) = U (mg/kg) x 12.35
U (mg/kg)	^{226}Ra (Bq/kg)	^{226}Ra (Bq/kg) = U (mg/kg) x 12.35
Th (mg/kg)	^{208}Tl (Bq/kg)	^{208}Tl (Bq/kg) = Th (mg/kg) x 4.063
K (%)	^{40}K (Bq/kg)	^{40}K (Bq/kg) = K (%) x 312.5

281

2.5. Data analysis

a) Influence of analytical techniques

The influence of the analytical techniques in the LIT database was assessed through a three-way Analysis of Variance (ANOVA) using the OGE classification scheme, the analytical techniques and LOI as categorical variables. The ANOVA design was unbalanced due to the unequal number of observations resulting from the level combinations of each factor (OGE, LOI and analytical techniques). Given an unbalanced design, the differences between the geochemical analysis techniques were assessed by pairwise comparisons of the Least square (LS) means calculated with the three-way ANOVA (the LS mean is an estimate of the population mean, gained from grouped data by adjusting for the influence of grouping, thereby adjusted for the imbalance of the ANOVA design). If the results of the pairwise comparison of the LS means show an agreement of the LS means between the different geochemical analysis techniques, the compiled database can be considered consistent within itself, thus, reliable. Data showing strong deviations from normality were transformed through the Box-Cox transformation (Zar, 2010).

b) Accuracy of the LIT database

One objective of the study is to evaluate whether the LIT database is accurate in the sense that mean geochemical concentrations per geological unit are representative for the units. Representativeness means that the frequency distribution of concentrations in samples is equal the true, but unknown one; in particular, the sample mean must be equal to the true mean. Deviation is called bias or inaccuracy. Since the true distributions

304   are not known, accuracy of samples cannot be validated by comparing sample and true

305   distributions. However, a necessary – though not sufficient – condition for accuracy is

306   that for each geological unit mean $TGDR_{calc}$ is equal (up to permitted tolerance) to mean

307    $TGDR_{obs}$ in the same unit, taken from the RMP.

308   As a first step, the arithmetic mean of the $TGDR_{obs}$ for each geological unit studied

309   of the OGE classification scheme (Table 1 and Figure 1) was estimated. The zonal

310   statistics tool in ArcGis 10.5.1 (ESRI, Redland CA, USA, 2017) was used for this

311   purpose. Given that the RMP data corresponds to data modelled by linear interpolation,

312   due to the absence of outliers, the arithmetic mean is a robust measure of central

313   tendency.Since the TGDR per pixel of the RMP are given as class values, i.e. belonging

314   to a class "i", $TGDR \in (x_i, x_{i+1})$, the AM cannot be simply calculated from pixel values.

315   This would be the straight-forward way, but the means per pixel are not available. An

316   approximation is the weighted mean of class means, $(x_{i-1}+x_i)/2$, with weight the number

317   of pixels $N(i-1, i)$ in this class divided by the total number of pixels, N. x_0 is set equal zero,

318   which is the physically possible lower bound of a geochemical concentration. The

319   question is how to deal with the highest class, labeled "$>x_n$", as no class mean can be

320   calculated, since its upper bound is not known. This can be done approximately by

321   assuming a tentative analytical model of the upper tail of the TGDR distribution and

322   calculate its contribution to the AM analytically. The maximum $TGDR_{obs}$ was estimated

323   by polynomial regression of the TGDR values displayed in the legend of the RMP (Batista

324   et al. 2013). Polynomials of degree 6 and 7 were applied to maximize the multiple R-

325   squared and minimize the residual standard error. A maximum $TGDR_{obs}$ of 236.911

326   nGy/h and 238.358 nGy/h were predicted from the 6-degree and 7-degree polynomial

327   regression model fittings, respectively. The mean value of 237.6 nGy/h was set as the

328   maximum $TGDR_{obs}$ in order to estimate the arithmetic means of $TGDR_{obs}$ for each

329   geological unit. We tried two additional tail models, but the results are very similar and

330   these models are not further discussed here.

331   As second step, the comparison of the arithmetic means between the LIT database

332   and the RMP for each geological unit was carried out using the Student's paired sample

333   t-test, the Wilcoxon median test and Pearson's correlation coefficient. The distributions

334   of $TGDR_{calc}$ and $TGDR_{obs}$ were compared with the Anderson-Darling and Kolmogorov-

335   Smirnov tests. Statistical analyses were performed with Statistica 7.0 (StatSoft Inc.,

336   USA) and R (Lenth, 2016; R Core Team, 2017).

337   **3. Results and discussion**

338   **3.1. Analysis of the influence of the analytical techniques on LIT database**

339   **a) Effect size**

340   The results of a three-away ANOVA performed on Box-Cox transformed data using

341   the OGE classification scheme, LOI and the analytical techniques as categorical

342   variables are shown in Table 3. The differences between the mean values of the

343   analytical techniques and geological factors were significant at a 0.001 level of

344   significance for U, Th, K and $TGDR_{calc}$. The effects of LOI were not significant at a 0.01

345   level of significance for U, Th, K and $TGDR_{calc}$.

346   The percentage of variation explained by the analytical techniques and LOI given by

347   the partial eta-squared was close to or lower than 2 %, being lower than the variance

348   explained by geological factors. According to Cohen's (1977) rule of thumb, the size of

349   the effects of the analytical techniques and particularly LOI can be considered small (<

350   2 %) while the size of the effects of the geological factors was large (> 14 %). The

351   variance explained by the LOI effects was generally lower than the variance explained

352   by the analytical techniques (Table 3). The size of the effects of the analytical techniques

353   was higher for the $TGDR_{calc}$ compared to the individual radioelements which is likely due

354   to the combination of analytical techniques that results in a higher number of categories,

355   hence, in a higher variability of geochemical analysis techniques used (Table 3).

356   The percentage of variation explained by geological factors was on average 53 % for

357   U, 38 % for Th, 50% for K and 51 % for the $TGDR_{calc}$. The variance explained by

358 geological factors was much higher than the variance explained by the analytical

359 techniques and LOI (Table 3). The geological factors are thereby the main source of

360 variability in the data, followed by the error component. The latter can be assumed to

361 mainly represent true spatial variability of geochemical concentrations – and in

362 consequence the calculated dose rate $TGDR_{calc}$ – within geological units.

363 **Table 3.** Summary table of a three-way ANOVA performed on U, Th, K and $TGDR_{calc}$

364 Box-Cox transformed data using the OGE classification, LOI and the analytical

365 techniques as categorical variables.

		SS	df	MS	F	p	Partial eta-squared (%)
U	OGE	2009.7	25	80.4	95.7	<0.001	52.7
	LOI	5.4	1	5.4	6.5	0.011	0.3
	Analytical techniques	33.0	2	16.5	19.7	<0.001	1.8
	Error	1801.1	2144	0.8			
Th	OGE	3457.9	26	133.0	58.70	<0.001	37.6
	LOI	0.9	1	0.9	0.38	0.536	<0.1
	Analytical techniques	37.9	2	18.9	8.35	<0.001	0.7
	Error	5741.2	2534	2.3			
K	OGE	1909.4	26	73.4	106.8	<0.001	50.4
	LOI	0.7	1	0.7	1.0	0.306	<0.1
	Analytical techniques	21.9	5	4.4	6.4	<0.001	1.2
	Error	1880.5	2735	0.7			
$TGDR_{calc}$	OGE	37380	25	1495	83.1	<0.001	50.7
	LOI	40	1	40	2.2	0.137	0.1
	Analytical techniques[a]	1882	9[a]	209	11.6	<0.001	4.9
	Error	36311	2018	18			

SS – Sum of squares; df – degrees of freedom; MS – Mean square; F – F-test; p – p-value.
[a]The effects of the group where U and Th were determined by NAA and K by AAS are not estimable for the $TGDR_{calc}$, thus were excluded from the analysis.

366 **b) Component effects**

367 The differences between the LS means of the analytical techniques were investigated

368 in Figure 2. The results of the pairwise comparison of the LS means are presented as

369 supplementary material for U, Th and K (Table A3) and $TGDR_{calc}$ (Table A4). The ICP-

370 MS LS mean was lower than the NAA and XRF means for both U and Th (Figure 2). For

371 U, the LS means for NAA and XRF were 35 % higher, on average, than the ICP-MS

372 mean. For Th, the XRF LS mean was 8 % higher while the NAA LS mean was 20 %

373 higher than the ICP-MS mean. The pairwise comparison of the LS means showed a

374 systematic statistically significant differences between the ICP-MS data compared to

375 other datasets (NAA and XRF) for U (Table A3). For Th, a statistically significant

376 difference was observed between NAA and ICP-MS datasets, however, the differences

377 between XRF and NAA, and XRF and ICP-MS were not significant (Table A3).

378   The analytical technique used to determine U was identical to the analytical technique

379 used to determine Th (ICP-MS, NAA or XRF in 2084 out of the 2173 observations

380 available for U (96% of the available data). As the ICP-MS LS means were generally

381 lower for both elements, a significant bias of this analytical technique is suggested. The

382 bias could be due to (1) a preference of the authors for analyzing rock samples with lower

383 U and Th concentrations with the ICP-MS technique; (2) lower detection limits achieved

384 by ICP-MS compared to other analytical techniques (e.g. Gill, 1997) or (3) by the

385 technique limitations such as an inefficient digestion of typically resistant U- and Th-

386 bearing minerals (e.g. zircon) or selective coprecipitation of these elements with fluorides

387 when hydrofluoric acid is used in the digestion process (Preusser and Kasper, 2001).

388   For K, the pairwise comparison of the LS means indicated a general agreement

389 between datasets apart from the observed statistically significant differences of the LS

390 means where K was determined by the ICP technique (Table A3). These results are

391 congruent with the observed LS mean of the ICP analysis technique which was 30 %

392 higher than the reference mean chosen (XRF, see Figure 2). Given that only 8 out of

393 2768 observations present a K concentration below the LLD, it is unlikely that the

394 observed difference could be caused by LLD values. Given that the ICP results were

395 retrieved from older literature sources (ex. Mitjavila et al. 1997; Ribeiro 1998; Table A1)

396 and that the ICP LS mean was higher than the reference mean chosen, the observed

397 difference could be due to lack of reporting of values below the LLD by the authors. Apart

398 from ICP and ICP-AES, deviations of the LS means from the reference mean chosen

399 were generally lower than 10 %.

400   The results of the pairwise comparison of the LS means for TGDR$_{calc}$ showed a

401   general agreement of the LS means between different geochemical analysis techniques

402   (Table A4). Statistically significant differences between the LS means were only

403   observed in 6 out of the 45 pairwise comparisons performed (Table A4). The compiled

404   database can thus be considered consistent within itself, hence reliable. Apart from the

405   dataset where K was determined by ICP-AES and ICP-MS, deviations of the LS means

406   from the reference mean chosen are equal to or lower than 10 %. The LS means where

407   U and Th data were acquired with ICP-MS are systematically lower than the LS means

408   where U and Th data were acquired with NAA and XRF, which is consistent with the

409   results observed for U and Th individually and can thus be caused by error propagation.

410   The LS means for the OGE units and LOI are presented as supplementary material

411   (Figures A1 and A2). The LS means display large differences between the various OGE

412   units for U, Th, K and TGDR$_{calc}$ (Figure A1), which are in accordance with the high

413   percentage of variation explained by the OGE classification system (Table 3). With

414   respect to LOI, higher LS means were expected in data corrected for the LOI and/or

415   volatile content (corresponding to effect named "FALSE"), as are observed for K and the

416   TGDR$_{calc}$ (Figure A2). However, lower LS means in LOI corrected data compared to

417   uncorrected data are observed for U and Th (Figure A2 in Supplementary material).

418   These results support the lack of a systematic influence of LOI. Given that the effects of

419   LOI are not significant for U, Th and K (Table 3), it can be concluded that the correction

420   of U, Th and K data for LOI or lack thereof does not affect significantly the results.

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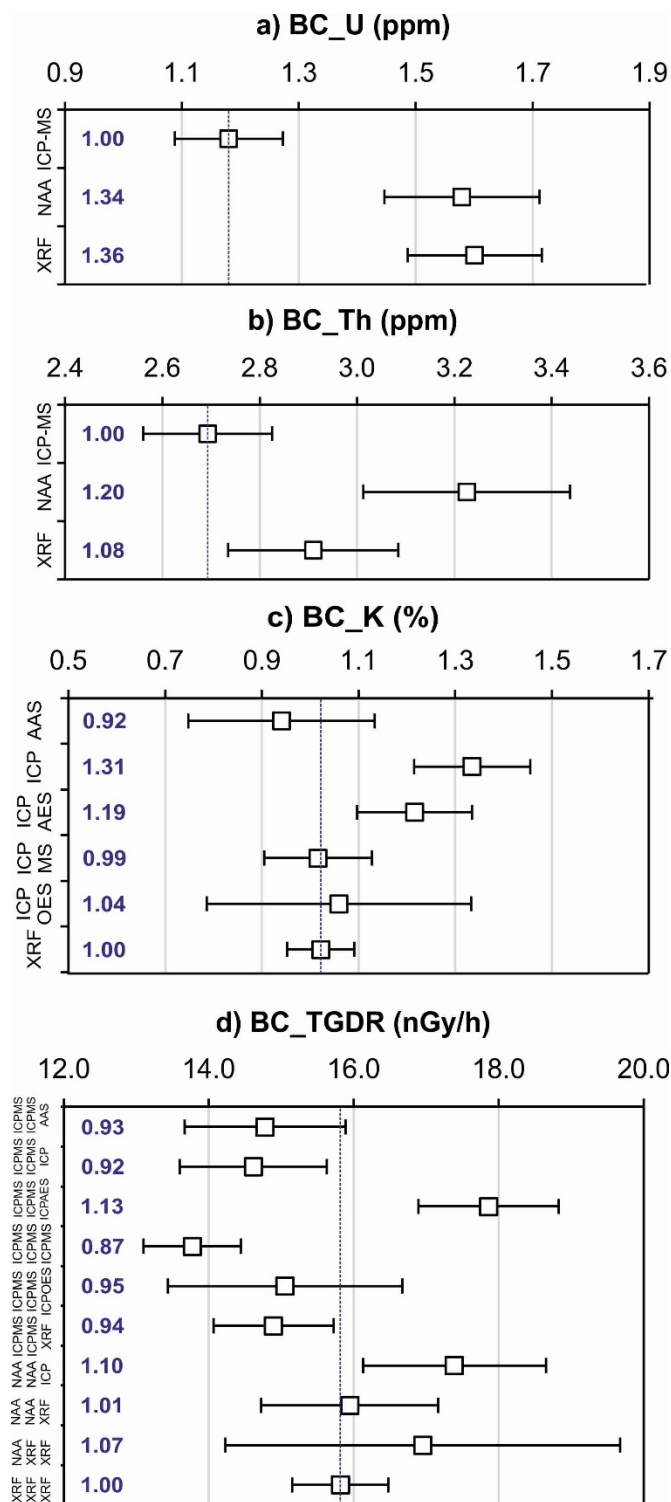
Figure 2. Plots of the least squares (LS) means of the analytical techniques effect for U, Th, K and $TGDR_{calc}$ Box-Cox transformed data. The bars indicate the 95% confidence interval of the LS mean. A LS mean was chosen as reference for comparison according to higher sample size and number of geological units sampled (see Tables A1 and A2, supplementary material). The proportion of the LS means were calculated assuming the ICP-MS mean as reference for U and Th; the XRF mean for K and the dataset where U, Th and K were determined by XRF for the $TGDR_{calc}$.

3.2. Variance component originating from spatial variability

In the previous analysis, variance has been attributed entirely to geology (component A, see section 1.4) and analytical techniques (B), while component C was ignored, i.e. possible lack of representativeness of data for a geological unit. A possible procedure for resolving this would be performing an even higher stage ANOVA including individual data sources (each consisting of a number of data) as additional classification variable, or as simplification, simple ANOVA for data sources within individual geological units and for same analytical technique. However, data are not sufficient for this.

The sources of the error terms in Table 3 are measurement uncertainty and probably dominantly, spatial variability within units. Its contribution to the SS (sum of squares) is in the same order of magnitude as the one due to OGE. Given the data situation, it is however difficult to say to which degree possibly unrepresentative samples from the variable population contribute to bias of the mean. The question deserves further investigation in the future.

3.3. Comparison of the LIT and RMP datasets

The arithmetic means of the $TGDR_{calc}$ from U, Th and K compiled data were compared to the $TGDR_{obs}$ for each geological unit in Figure 3 and Table 4. The correlation between $TGDR_{calc}$ and $TGDR_{obs}$ was highly significant ($p < 0.001$). The results of a paired sample t-test and Wilcoxon median tests indicate that the differences between the arithmetic means of $TGDR_{calc}$ and $TGDR_{obs}$ were not statistically significant ($p = 0.126$ and $p = 0.14$, respectively). Distributions of $TGDR_{calc}$ and $TGDR_{obs}$ were about equal according to Kolmogorov-Smirnov and Anderson-Darling tests. If deviation from $TGDR_{obs}$ by pooled standard deviation (SD) is taken as criterion, 14 out of 26 OGE units are located within one pooled SD around $TGDR_{obs}$ (dashed lines in Figure 3), only 1 out of 26 is located outside 2 pooled SDs.

(The pooled SD is defined as

$$s_{pooled} = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \cdots + (n_k - 1)s_k^2}{n_1 + n_2 + \cdots + n_k - k}} \qquad (2)$$

with s_i the individual SDs and n_i the number of data in OGE unit (i). Its value is 29 nGy/h.)

A systematic overestimation of the TGDR$_{calc}$ compared to TGDR$_{obs}$ was observed for the sedimentary rocks (N2, N1c, K1-2, K1, TJ1 and the C2 units) coupled with absolute differences of the TGDR$_{calc}$ generally higher than 29 nGy/h (the pooled SD of the RMP dataset; Table 4, Figure 3). This effect may be caused, by (1) the lack of spatial representativeness of the data (as sampling of stratigraphic sequences is commonly carried out along vertical profiles instead of spatial grids) or (2) the lack of data from carbonate rocks. Carbonate rocks are a common subordinate lithology of the abovementioned geological units (see Table 1), presenting average radionuclides concentrations generally lower than siliciclastic rocks (e.g. Sêco et al. 2016).

Table 4. Comparison of the arithmetic means (± standard deviation) of the TGDR between LIT (TGDR$_{calc}$) and the RMP datasets (TGDR$_{obs}$).

Group	OGE unit	TGDR$_{calc}$ [1]	TGDR$_{obs}$ [2]	Difference [2] − [1]
Sedimentary rocks	N2	78 ± 26	32 ± 19	-46
	N1c	70 ± 23	36 ± 22	-34
	K1-2	106 ± 21	42 ± 28	-63
	K1	73 ± 21 [b]	46 ± 21	-27
	TJ1	85 ± 29	44 ± 20	-41
	C2	94 ± 15	59 ± 34	-35
Metamorphic rocks	C1-2	78 ± 27 [b]	65 ± 14	-13
	SDof	71 ± 18	19 ± 13	-52
	SD	39 ± 41	90 ± 22	51
	SDP	107 ± 37 [b]	91 ± 21	-16
	ODP	81 ± 58 [b]	104 ± 34	23
	O_a	69 ± 38 [b]	88 ± 27	18
	gz	77 ± 25 [b]	87 ± 28	10
	Npep	82 ± 23 [b]	80 ± 29	-2
	NP2	46 ± 30 [b]	60 ± 21	14
	NP1	31 ± 31 [b]	56 ± 29	25
Igneous rocks	gama2	68 ± 35 [b]	63 ± 16	-4
	CVL	52 ± 23	14 ± 10	-38
	g1_b	194 ± 101 [b]	157 ± 39	-37
	g2_b	137 ± 59 [b]	172 ± 40	35

	g3	157 ± 52[b]	142 ± 46	-15
	g1_a	157 ± 88[b]	136 ± 32	-21
	g2_a	150 ± 49[b]	121 ± 24	-29
	g1a	61 ± 34[b]	62 ± 23	1
	gama	9 ± 10	51 ± 19	43
	D3C1	50 ± 40[b]	75 ± 26	25

[a]$TGDR_{obs}$ was calculated assuming an arbitrary maximum $TGDR_{obs}$ of 237.6 nGy/h.
[b]The $TGDR_{calc}$ is located within one pooled SD of the $TGDR_{obs}$.

469   The arithmetic means of the $TGDR_{calc}$ of granitic rocks are also generally

470   overestimated in LIT database (g1_b, g3, g1_a and g2_a). In this case, the limitations of

471   the RMP data must be taken into account, namely the fact that the maximum $TGDR_{obs}$

472   in mainland Portugal is unknown. A value of 237.6 nGy/h was set as the maximum

473    $TGDR_{obs}$ in order to compute the mean $TGDR_{obs}$ by geological unit. This issue only

474   affects the geological units which display a $TGDR_{obs}$ higher than 216.2 nGy/h, which are

475   listed in Table 5 and include the abovementioned granitic rocks (g1_b, g2_b, g3, and

476   g1_a). These units present a high percentage of their area (> 3 %) characterized by a

477    $TGDR_{obs}$ above 216.2 nGy/h. The underestimation of $TGDR_{obs}$ of these units may be

478   caused by the underestimation of the maximum $TGDR_{obs}$ chosen (of 237.6 nGy/h),

479   biasing the estimation mean $TGDR_{obs}$ by geological unit.

480   **Table 5.** Percentage of the area characterized by a $TGDR_{obs}$ higher than 216.2 nGy/h.

	OGE units	% of Area
Sedimentary rocks	N2	0.01
	N1c	0.05
	K1_2	0.68
	ODP	1.20
Metamorphic rocks	O_a	0.16
	gz	0.06
	NPep	0.47
Igneous rocks	g1_b	5.36
	g2_b	15.15
	g3	9.54
	g1_a	3.04
	g2_a	0.37

481   From a health perspective, the overestimation of the $TGDR_{calc}$ is not as concerning

482   as its underestimation, which was observed systematically in the SD, g2_b and the gama

483   units. In the case of the g2_b unit, the difference observed between the $TGDR_{calc}$ for

484 Model 1 is, however allocated within one SD of the $TGDR_{obs}$. The underestimation of the

485 $TGDR_{calc}$ of the g2_b may be due to the underrepresentation of quantitative data from

486 metallogenic deposits of uranium and/or radium that are common in the g2_b unit (ex.

487 Marques et al. 2010; Neiva et al. 1987; Trindade et al. 2013). Because the g2_b dataset

488 corresponds to one of the largest datasets available (Table A1, Supplementary material),

489 this enforces the hypothesis that the major source of error within the compiled database

490 was the insufficient representativeness of the data, which leads to a biased estimate of

491 the mean, rather than the amount of data or the analytical techniques. Apart from the SD

492 and SDof units, the absolute deviations between the arithmetic means of $TGDR_{calc}$ and

493 $TGDR_{obs}$ were generally lower than 29 nGy/h for the metamorphic rocks (Table 4). For

494 the SD unit, the only dataset available was retrieved from Dahn et al. (2014) and refers

495 to mafic rocks outcropping in the SD unit. Thus, the underestimation of the $TGDR_{calc}$

496 reflects the lack of data from other types of rocks within the unit, particularly of the

497 predominant lithology of the unit namely phyllites (Table 1). The underestimation of the

498 $TGDR_{calc}$ of the gama unit may be due to the lack of data from differentiated rocks, such

499 as anorthositic rocks and diorites (the subordinate lithologies of the gama unit, Table 1)

500 that may present higher contents of terrestrial radionuclides than gabbros as U, Th and

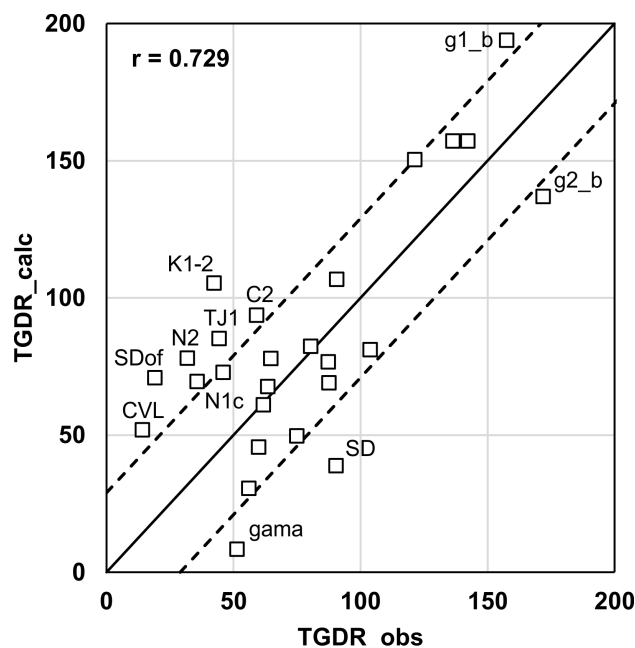501 K become enriched with magmatic differentiation (Heier and Rogers, 1963).

502

503   **Figure 3.** Scatterplot of the arithmetic means of the TGDR (in nGy/h) of each geological

504   unit. The dashed lines indicate deviations of 29 nGy/h (the pooled SD) from the identity

505   line.

506   The pooled SD of the RMP dataset was set as criterion to appraise the discrepancy

507   between the arithmetic means of the RMP and LIT databases. Given the statistical

508   parameters of the differences between $TGDR_{calc}$ and $TGDR_{obs}$ and their distributions, the

509   compatibility of the RMP and LIT databases can be considered acceptable, but not

510   perfect. For some geological units, the exact reason for discrepancy remains to

511   investigated, in order to improve further attempts of the kind.

512   As the $TGDR_{calc}$ was calculated from U, Th and K data compiled from scientific

513   literature, the compatibility of the TGDR between the LIT and the RMP datasets (namely,

514     $TGDR_{calc}$ and $TGDR_{obs}$) implies that the estimation of the contents of the terrestrial

515   radionuclides in bedrock from compiled datasets is also reasonable. Putting it more

516   precisely, since the approximate equality of $TGDR_{calc}$ and $TGDR_{obs}$ is only a necessary

517   condition for the hypothesis to be true that the LIT database represents U, Th and K

518   concentration in rocks reasonably well, the result of this investigation does not reject the

519   hypothesis.

520   Vein-type rocks were excluded from the comparison exercise of LIT and RMP

521   databases due to their large perimeter to area ratio. Given the compatibility of the RMP

522   and LIT datasets, the $TGDR_{calc}$ of vein-type rocks was estimated resorting to data

523   compiled from local geochemical surveys. The mean $TGDR_{calc}$ for the f1 and f2 (basic

524   veins) and qz (quartz veins) units are presented in Table 6. The $TGDR_{calc}$ of basic vein-

525   type rocks (f1 and f2) is similar to other mafic rocks units (ex. CVL, gama, and SDof units,

526   Tables 1 and 4) as expected. Quartz veins present a similar $TGDR_{calc}$ to sedimentary

527   and metamorphic rocks, being lower than the average $TGDR_{calc}$ of granitic rocks (Tables

528   1 and 4).

529   **Table 6.** Estimation of the TGDR of vein-type units using LIT data.

	OGE units	Number of samples	TGDR$_{calc}$ (nGy/h) Mean	TGDR$_{calc}$ (nGy/h) Standard deviation	References
Vein-type rocks	f1	26	14	5	Cebriá et al. (2003); Martins (1999); Martins et al. (2009); Youbi et al. (2003);
	f2	17	34	14	Trindade et al. (2013); Alves (2010);
	qz	16	83	20	Lima (2000)

4. Conclusions

Two databases were compared with the aim of validating the compilation of literature data to estimate the mean concentrations of terrestrial radionuclides in bedrock using geological units as reference units. The results show that the compatibility of the databases was essentially reasonable. The differences between the arithmetic means were generally lower than the maximum allowable discrepancy set and the differences between the two databases were not statistically significant. A systematic overestimation of the contents of radionuclides calculated from the compiled data and observed in sedimentary rocks probably reflects the lack of representativeness of the data compiled for these units, while the differences observed for some granitic rocks may reflect the limitations of the TGDR$_{obs}$. Despite the significance of the effects of the analytical techniques, the variance explained by them, ranging from less than 1% to 5%, is sufficiently low, thereby lacking a significant impact on the comparability of the results acquired with different analytical techniques. The major sources of variability in the data are geological factors as demonstrated by the high percentage of variation explained by this factor in the ANOVA computed, as well as the true spatial variability of geochemical concentrations within geological units.

Geochemical characterization of geological units based on scattered literature data, as attempted in this study, allows the development of maps of terrestrial radionuclides contents in bedrock without large-scale sampling efforts, since a large amount of data is already available. Where extensive TGDR surveys are available, validation may be repeated e.g. along the lines presented here.

While the estimates computed for some units may be unreliable, they also set the groundwork needed to support further research. Certainly, a key problem is representativeness of the data, on which depends the reliability of the estimates of the mean contents of U, Th and K per geological units. It can be improved when more data with better coverage of geological units are available. Nonetheless, we think that generation of maps of U, Th and K concentrations in rock based on geological units is feasible.

Acknowledgements

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Supplementary material

Table A1. Summary of the data available in LIT database for the OGE units sampled by

geological unit. 2173 observations were compiled for U, 2564 for thorium and 2768 for K

acquired with 7 different analytical techniques.

OGE unit	Analytical Technique[a]	N (U)	N (Th)	N (K)	References
C1-2	ICP-MS	74	74	0	Jorge et al. (2013); Trindade (2007)
	ICP-OES	0	0	74	
	NAA	7	7	0	
	XRF	0	0	7	
C2	ICP-MS	18	20	18	Dinis et al. (2011); Ribeiro et al. (2010)
	XRF	0	0	2	
CVL	ICP-MS	62	62	62	Miranda (2010); Miranda et al. (2009)
D2-3	XRF	0	30	32	Boulter et al. (2004)
D3C1	ICP	0	0	59	Boulter et al. (2004); Mitjavila et al. (1997); Rosa et al. (2004, 2006); Schützet al. (1987)
	NAA	59	129	0	
	XRF	28	27	135	
g1_a	AAS	0	0	17	Coelho et al. (2007); Costa et al. (2014); Ferreira (2013); Godinho et al. (1986, 1991); Gomes (1989); Gomes and Neiva (2002, 2005); Gomes et al. (2011, 2013); Neiva and Gomes, (1991); Neiva et al. (2008, 2009); Neves et al. (1999); Silva (2000, 2014a); Teixeira (2008); Teixeira et al. (2012)
	ICP	0	0	32	
	ICP-AES	0	0	7	
	ICP-MS	77	77	0	
	NAA	4	13	0	
	XRF	150	205	230	
g1_b	ICP-AES	0	0	15	Costa (2011); Costa et al. (2014); Gomes and Neiva (2005);
	ICP-MS	15	15	0	
	NAA	6	6	0	
	XRF	0	0	6	
g1a	ICP-AES	0	0	22	Antunes et al. (2010); Lima et al. (2013, 2014); Moita et al. (2009)
	ICP-MS	57	79	57	
g2_a	ICP-AES	0	0	12	Cerejo (2013); Neves et al. (2007); Silva and Neiva (1990)
	ICP-MS	12	12	0	
	NAA	10	10	0	
	XRF	8	8	18	
g2_b	AAS	0	0	43	Antunes (2006); Antunes et al. (2008, 2013); Carvalho et al. (2012); Costa (2006, 2011); Godinho et al. (1991); Lima et al. (2013, 2014); Marques et al. (2010); Martins et al. (2013); Neiva et al. (1987, 2009, 2011a, 2011b); Ramírez and Grundvig (2000); Silva (2014b); Silva et al. (2000); Trindade et al. (2013); van der Weijden and van der Weijden (1995)
	ICP-AES	0	0	134	
	ICP-MS	165	164	24	
	NAA	23	13	0	
	XRF	185	259	281	
g3	ICP-AES	0	0	64	Costa (2006, 2011); Gomes (2008); Jaques et
	ICP-MS	56	56	6	

OGE unit	Analytical Technique[a]	N (U)	N (Th)	N (K)	References
	NAA	0	3	0	al. (2016); Martins et al. (2009); Neiva (1993); Neves and Pereira, (2007); Ramírez and Menéndez (1999)
	XRF	14	14	32	
GAMA	ICP	0	0	60	Caldeira et al. (2007); Jesus et al. (2014, 2016); Pedro (2004); Quesada et al. (1994)
	ICP-MS	92	97	138	
	NAA	32	32	0	
	XRF	0	0	15	
GAMA2	ICP-MS	16	16	16	Grange et al. (2010); Miranda (2010)
gz	ICP-MS	8	8	4	Antunes (2006); Antunes et al. (2009); Cruz (2007); Godinho et al. (1986); Neves et al. (1998); Pereira et al. (2006, 2011); Sánchez-García et al. (2010, 2013)
	XRF	25	57	62	
K1	NAA	52	52	0	Trindade (2007); Trindade et al. (2010)
	XRF	0	0	52	
K1-2	ICP-MS	45	45	0	Dinis et al. (2016)
	XRF	0	0	45	
N1c	ICP	0	0	32	Arribas et al. (2014); Bustillo et al. (2012); Lisboa et al. (2015); Marques et al. (2010); Reis et al. (2012)
	ICP-AES	0	0	5	
	ICP-MS	48	48	0	
	NAA	16	16	0	
	XRF	0	0	16	
N2	ICP-MS	45	72	5	Dinis and Oliveira (2016); Dinis et al. (2011); Pereira et al. (2006); Trindade (2007)
	NAA	6	6	0	
	XRF	0	0	88	
NP1	ICP-AES	0	0	69	Gómez-Pugnaire et al. (2013); Henriques et al. (2017); Silva (2007)
	ICP-MS	90	90	0	
	XRF	0	0	21	
NP2	ICP	0	0	14	Dinis et al. (2011); Henriques et al. (2006, 2016); Lorda et al. (2013); Pereira et al. (2006, 2011)
	ICP-AES	0	0	5	
	ICP-MS	16	63	42	
	XRF	1	1	3	
Npep	AAS	0	0	16	Aires et al. (2011); Candeias et al. (2015); Cerejo (2013); Coelho et al. (2007); Dinis et al. (2011); Fuenlabrada et al. (2016); Godinho et al. (1991); Marques et al. (2010); Neves et al. (1999); Noronha et al. (2012); Oliveira (2015); Pinto (2014); Ribeiro (1998); Silva (2014a); Trindade et al. (2013); Ugidos et al. (1997a, 1997b, 2003a, 2003b, 2010); Valladares et al. (2000, 2002); Villaseca et al. (2014)
	ICP	0	0	35	
	ICP-AES	0	0	176	
	ICP-MS	310	341	86	
	ICP-OES	0	0	24	
	NAA	9	9	0	
	XRF	22	22	30	
O_a	ICP	0	0	1	Oliveira (2015); Pereira et al. (2011); Ribeiro et al. (2010); Silva (2014a)
	ICP-MS	2	2	1	
	XRF	15	15	15	
ODP	ICP	0	0	52	Dias (2011); Noronha et al. (2012); Ribeiro (1998)
	ICP-MS	41	41	0	
	NAA	46	46	0	
	XRF	6	6	47	
SD	XRF	33	33	33	Dahn et al. (2014)

OGE unit	Analytical Technique[a]	N (U)	N (Th)	N (K)	References
SDof	AAS	0	0	5	Fuenlabrada et al. (2010, 2012); Teixeira et al. (2010)
	ICP-MS	48	43	0	
	ICP-OES	0	0	43	
SDP	ICP	0	0	60	Noronha et al. (2012); Ribeiro (1998)
	NAA	54	55	0	
	XRF	3	3	3	
TJ1	NAA	62	62	0	Trindade (2007); Trindade et al. (2010)
	XRF	0	0	60	

N – number of observations.
[a]ICP-MS – Inductively Coupled Plasma Mass Spectrometry; ICP-OES – Inductively Coupled Plasma Optical Emission Spectrometry; NAA – Neutron Activation Analysis; XRF – X-Ray Fluorescence; ICP - Inductively Coupled Plasma; ICP-AES – Inductively Coupled Plasma Atomic Emission Spectrometry; AAS – Atomic Absorption Spectrometry.

1033

1034 **Table A2.** Summary of the data available by analytical technique.

	Analytical technique			Number of samples (N)	% N	Number of OGEs sampled	%OGE
	U	Th	K				
U	NAA			386	17.8	14	51.9
	XRF			490	22.5	12	44.4
	ICP-MS			1297	59.7	21	77.8
Th		NAA		459	17.9	15	55.6
		XRF		680	26.5	13	48.1
		ICP-MS		1425	55.6	21	77.8
K			AAS	81	2.9	4	14.8
			ICP-OES	141	5.1	3	11.1
			ICP-MS	459	16.6	12	44.4
			ICP	345	12.5	9	33.3
			ICP-AES	509	18.4	10	37.0
			XRF	1233	44.5	23	85.2
TGDR$_{calc}$[a]	ICP-MS	ICP-MS	ICP-MS	330	16.1	12	44.4
	ICP-MS	ICP-MS	ICP-OES	141	6.9	3	11.1
	ICP-MS	ICP-MS	ICP	143	7.0	5	18.5
	NAA	NAA	ICP	176	8.6	5	18.5
	NAA	NAA	XRF	160	7.8	8	29.6
	XRF	XRF	XRF	421	20.5	11	40.7
	ICP-MS	ICP-MS	XRF	217	10.6	10	37.0
	ICP-MS	ICP-MS	ICP-AES	380	18.5	8	29.6
	ICP-MS	ICP-MS	AAS	76	3.7	3	11.1
	NAA	XRF	XRF	10	0.5	1	3.7

[a]The analytical techniques listed for the TGDR$_{calc}$ refer to the compilation of the analytical techniques used to analyse U, Th and K.

1035

1036 **Table A3.** Pairwise comparison of the LS means of the analytical techniques for U, Th

1037 and K. P-values were adjusted with the false discovery rate (FDR) method (Lenth, 2016).

	Analytical techniques under comparison	Difference between the LS means	SE	t	p
U	NAA x ICP-MS	-0.399	0.085	-4.691	<0.001(*)
(df =	NAA x XRF	-0.022	0.091	-0.240	0.9688
2144)	ICP-MS x XRF	-0.421	0.075	-5.589	<0.001(*)
Th	NAA x ICP-MS	-0.532	0.132	-4.033	<0.001(*)
(df =	NAA x XRF	0.316	0.145	2.171	0.076
2534)	ICP-MS x XRF	-0.217	0.115	-1.890	0.142
	AAS x ICP	-0.394	0.116	-3.411	0.009(*)
	AAS x ICP-AES	-0.276	0.112	-2.469	0.134
	AAS x ICP-MS	-0.076	0.114	-0.667	0.986
	AAS x ICP-OES	-0.119	0.169	-0.708	0.981
	AAS x XRF	-0.081	0.099	-0.822	0.964
	ICP x ICP-AES	0.119	0.076	1.562	0.624
K	ICP x ICP-MS	0.319	0.077	4.163	0.001(*)
(df =	ICP x ICP-OES	0.275	0.155	1.770	0.485
2735)	ICP x XRF	0.313	0.067	4.664	<0.001(*)
	ICP-AES x ICP-MS	0.200	0.075	2.674	0.081
	ICP-AES x ICP-OES	0.156	0.148	1.055	0.899
	ICP-AES x XRF	0.194	0.066	2.923	0.041
	ICP-MS x ICP-OES	-0.044	0.154	-0.282	1.000
	ICP-MS x XRF	-0.006	0.071	-0.078	1.000
	ICP-OES x XRF	0.038	0.151	0.253	1.000

SE – standard error; t, *p* – t-test and respective p-value. Significant values at $\alpha = 0.01$ are indicated with (*).

1038

Table A4. Pairwise comparison of the LS means of the analytical techniques for TGDR$_{calc}$
(df = 2018). P-values were adjusted with the false discovery rate (FDR) method (Lenth, 2016).

Analytical techniques[a] under comparison							Difference between the LS means	SE	t	p
U	**Th**	**K**		**U**	**Th**	**K**				
ICP-MS	ICP-MS	AAS	x	ICP-MS	ICP-MS	ICP	0.162	0.780	0.208	1.000
				ICP-MS	ICP-MS	ICP-AES	-3.082	0.761	-4.052	0.002(*)
				ICP-MS	ICP-MS	ICP-MS	1.005	0.653	1.538	0.877
				ICP-MS	ICP-MS	ICP-OES	-0.275	1.058	-0.260	1.000
				ICP-MS	ICP-MS	XRF	-0.118	0.712	-0.166	1.000
				NAA	NAA	ICP	-2.611	0.900	-2.902	0.106
				NAA	NAA	XRF	-1.168	0.888	-1.316	0.950
				NAA	XRF	XRF	-2.175	1.434	-1.517	0.886
				XRF	XRF	XRF	-1.038	0.544	-1.907	0.664
ICP-MS	ICP-MS	ICP	x	ICP-MS	ICP-MS	ICP-AES	-3.245	0.516	-6.289	<0.001(*)
				ICP-MS	ICP-MS	ICP-MS	0.842	0.561	1.501	0.892
				ICP-MS	ICP-MS	ICP-OES	-0.437	0.901	-0.485	1.000
				ICP-MS	ICP-MS	XRF	-0.280	0.587	-0.478	1.000
				NAA	NAA	ICP	-2.774	0.786	-3.530	0.015
				NAA	NAA	XRF	-1.330	0.798	-1.668	0.814
				NAA	XRF	XRF	-2.338	1.498	-1.560	0.867
				XRF	XRF	XRF	-1.200	0.630	-1.906	0.665
ICP-MS	ICP-MS	ICP-AES	x	ICP-MS	ICP-MS	ICP-MS	4.087	0.527	7.749	<0.001(*)
				ICP-MS	ICP-MS	ICP-OES	2.807	0.828	3.392	0.025
				ICP-MS	ICP-MS	XRF	2.964	0.545	5.439	<0.001(*)
				NAA	NAA	ICP	0.471	0.778	0.606	1.000
				NAA	NAA	XRF	1.914	0.782	2.448	0.298
				NAA	XRF	XRF	0.907	1.482	0.612	1.000
				XRF	XRF	XRF	2.045	0.616	3.318	0.031
ICP-MS	ICP-MS	ICP-MS		ICP-MS	ICP-MS	ICP-OES	-1.280	0.895	-1.429	0.918
				ICP-MS	ICP-MS	XRF	-1.123	0.555	-2.024	0.582
				NAA	NAA	ICP	-3.616	0.760	-4.759	<0.001(*)
				NAA	NAA	XRF	-2.173	0.751	-2.894	0.108
				NAA	XRF	XRF	-3.180	1.429	-2.225	0.440
				XRF	XRF	XRF	-2.042	0.492	-4.155	0.001(*)
ICP-MS	ICP-MS	ICP-OES	x	ICP-MS	ICP-MS	XRF	0.157	0.932	0.168	1.000
				NAA	NAA	ICP	-2.336	1.074	-2.176	0.474
				NAA	NAA	XRF	-0.893	0.988	-0.903	0.996
				NAA	XRF	XRF	-1.900	1.661	-1.144	0.980
				XRF	XRF	XRF	-0.763	0.963	-0.792	0.999
ICP-MS	ICP-MS	XRF	x	NAA	NAA	ICP	-2.493	0.695	-3.586	0.013
				NAA	NAA	XRF	-1.050	0.782	-1.343	0.944
				NAA	XRF	XRF	-2.057	1.456	-1.413	0.924
				XRF	XRF	XRF	-0.920	0.542	-1.696	0.798
NAA	NAA	ICP	x	NAA	NAA	XRF	1.443	0.944	1.528	0.881
				NAA	XRF	XRF	0.436	1.558	0.280	1.000
				XRF	XRF	XRF	1.574	0.769	2.047	0.566
NAA	NAA	XRF	x	NAA	XRF	XRF	-1.007	1.552	-0.649	1.000
				XRF	XRF	XRF	0.130	0.764	0.170	1.000
NAA	XRF	XRF	x	XRF	XRF	XRF	1.137	1.375	0.827	0.998

SE – standard error; t, *p* – t-test and respective p-value. Significant values at α = 0.01 are indicated with (*). [a]The analytical techniques listed for the TGDR$_{calc}$ refer to the compilation of the analytical techniques used to analyse U, Th and K.

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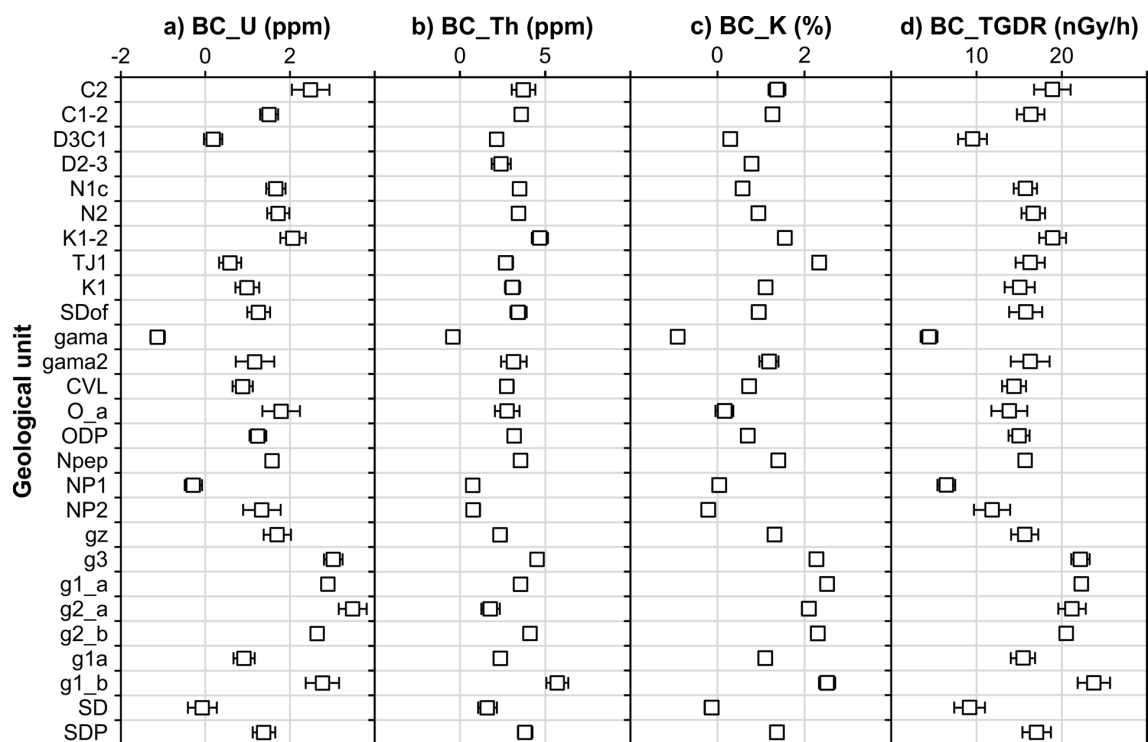1043   **Table B1.** Compiled geochemical database.

Figure A1. Plots of the least squares (LS) means of the OGE effect for U, Th, K and TGDR$_{calc}$ Box-Cox (BC) transformed data by geological unit. The bars indicate the 95% confidence interval of the LS mean.
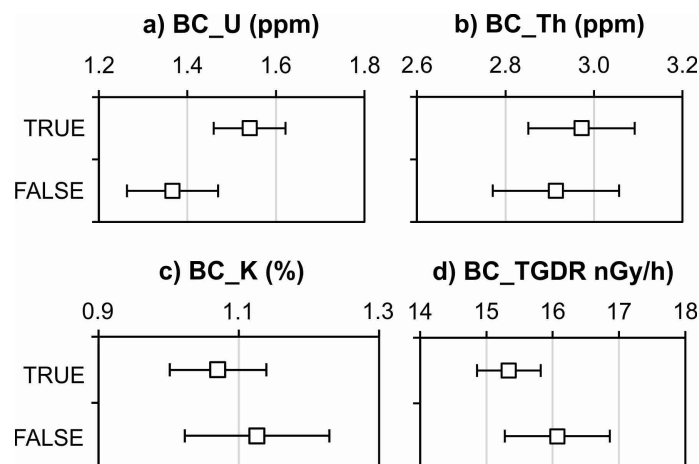

Figure A2. Plots of the least squares (LS) means of the LOI effect for U, Th, K and TGDR$_{calc}$ Box-Cox (BC) transformed data. The bars indicate the 95% confidence interval of the LS mean. Each observation of U, Th, K and TGDR$_{calc}$ is classified as "true" if the authors estimated but did not corrected the data for LOI (or the volatile content) and "false" otherwise.