1 Trace element concentrations in mineral phosphate fertilizers used in

2 Europe: a balanced survey

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13 Abstract

14 Mineral phosphate (P) fertilizers contain trace elements (TE) and can be a long-term source of these elements in soil. This study aimed to survey TE concentrations in mineral P fertilizers 15 16 consumed in 25 of the EU-28 countries plus Norway (EU-28+1), to improve estimates of the 17 EU wide input of TEs in agricultural soils. Different mineral P fertilizers (n = 414) were 18 collected from EU-28+1 with a consumption-balanced sampling strategy. The samples were analyzed by ICP-MS for 21 elements (Na, Mg, Al, P, S, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, 19 20 As, Mo, Cd, Pb, Sb and U) that had adequate analytical quality control. Trace element 21 concentrations in the P fertilizers were positively correlated with the P content for Cd, U, V, 22 Sb, Cr, As and Ni. In addition, two groups of rock P are likely the basis of P fertilizers in EU-23 28+1, i.e., with a high TE/P (n = 288) and low TE/P ratio (n = 126). The TE concentrations, 24 relative to the aqua regia soluble concentration in EU arable soils, were highest for U, followed 25 by Cd and then by other TEs. The Cd and U concentrations showed strong association but suggest that rock phosphates with two different Cd/U ratio are used. The Cd/P2O5 ratio varied 26 significantly among countries and averaged 28 mg Cd kg⁻¹ P₂O₅. An EU weighted mean is 30 27 mg Cd kg⁻¹ P₂O₅, based on country average data and P consumption. Both means are below 28 29 earlier EU estimates, likely because of sampling bias in those surveys. About 11% of the 30 fertilizers exceed the current European Cd limit (60 mg Cd kg⁻¹ P₂O₅). This survey illustrates 31 the importance of a consumption-balanced sampling strategy to estimate TE inputs at a large scale and provides the data necessary for risk assessment of TEs in agricultural soils. 32

33 Key words: mineral P fertilizers, trace elements, soils, risk assessment, cadmium, uranium

35 **1. Introduction**

Mineral phosphate (P) fertilizers contain several trace elements (TE) that are added to soil when 36 37 these fertilizers are spread. As such, P fertilizers become an important source of these TEs to 38 agricultural soils and, eventually, the food chain. Most of the TEs present in agricultural soils 39 are derived from fertilizing with rock-phosphate, since nitrogen and potassium fertilizers are 40 low in TEs (McBride and Spiers, 2001). The TE concentrations in the rock phosphate vary by 41 origin, i.e., low TE concentrations are found in igneous P rocks and high concentrations in 42 sedimentary P rocks (Kratz et al., 2016). For example, typical low cadmium (Cd) rock phosphates (<100 mg Cd kg⁻¹ P) are those from Florida and Russia (Kola) whereas many rock 43 44 phosphates from Africa (Morocco, Togo) contain average to high Cd concentrations (100 – 350 mg Cd kg⁻¹ P; McLaughlin et al. (1996)). 45

46 The potential of trace element enrichment in soil by long-term mineral P fertilizer application 47 depends on the concentrations of the trace elements in the fertilizer relative to the soil 48 background concentrations. In 1992, Sauerbeck compared element concentrations in rock 49 phosphates with earth crust averages, and concluded that only As, Cd, Cr, F, Sr, Th, U, Zn and 50 the rare earth elements La and Nd, have a potential risk to accumulate in soil by mineral P 51 fertilizer application. Taking also harvest offtake into account, mass balance calculations for 52 Australian soils show that the TE enrichment due to P fertilizer application, relative to natural 53 soil background, follows the sequence Cd>F>Hg>As~Pb (McLaughlin et al., 1996). Finally, 54 due to their toxicity, As, Cd and Pb concentrations in mineral P fertilizers should be closely monitored, however, the potential enrichment by mineral P fertilizer applications is highest for 55 56 Cd, due to the general lower soil concentration of Cd compared to As and Pb (Jiao et al., 2012).

57 The TE enrichment in soil is most documented for Cd and identified first in Australia (Williams 58 and David, 1973). In addition, archived soil samples dating back to 1850 from Rothamsted 59 Research (UK) showed that long-term P fertilizer application has been a source of Cd to soil in 60 the UK (Jones et al., 1987), while no evidence for enrichment through mineral P fertilization 61 was found for all other elements tested in these long-term P trials (i.e., Co, Cr, Cu, Mo, Ni, Pb, Rb, Sr, V, Y, Zn and Zr; (Jones and Symon, 1987)). Similar trends in Cd enrichment have been 62 63 found in other long-term P fertilizer trials in European countries like Denmark and France (Juste and Tauzin, 1986; Tjell and Christensen, 1985). In addition to Cd, the P fertilizers have been 64 found to be also an important source of uranium (U) in soils. First demonstrations of U 65 accumulation were found in the soils of Rothamsted Research (UK) where ~100 years of P 66 67 fertilization increased topsoil U concentrations relative to values observed at the start of the long-term field experiments or relative to the values measured in the no-P treatment (Rothbaum 68 69 et al., 1979). The accumulation of U was also detectable in plots in France that had been 70 amended with P fertilizers for 15 - 30 years and corresponding trends in thorium (Th) were also 71 found, although less apparent than those of U (Wetterlind et al., 2012). A collation of data from 72 Germany showed U accumulation in long-term plots ranging between undetectable to 0.4 mg U kg⁻¹ (Rogasik et al., 2008). A trend analysis of total soil Cd and U at six fertilized sites in 73 74 Switzerland showed no detectable changes over 25 years in total soil Cd in contrast to positive trends in total soil U (an increase of 0.1 - 0.7 mg U kg⁻¹ soil) at four of the six sites (Bigalke 75 76 et al., 2017). In the study of Schipper et al. (2011) however, the TE accumulation in the soil of 77 a long-term field trial, relative to initial soil concentrations, was greater for Cd during the initial 78 6 years of trial and greater for U during the following 17 years. Interestingly, this change in TE 79 accumulation rate over time coincided with a change in mineral P fertilizer use in that trial, i.e. from a single superphosphate to a triple superphosphate fertilizer. 80

81 Consequently, Cd and U have likely the highest enrichment potential, due to the combination 82 of high concentrations present in P rocks and subsequent produced fertilizers, relative to the 83 low background concentrations in soils. A good estimate of the TE concentrations in mineral 84 fertilizers will thus be an important aspect for risk assessment and it has become critical in the

debate about the Cd limits in Europe that was concluded in 2019 at a limit of 60 mg Cd kg⁻¹ 85 86 P₂O₅ (EU, 2019; Ulrich, 2019). To evaluate the risk at a large scale, surveys should be 87 comprehensive and sample the major sources. A world-wide survey of Cd concentrations in P-88 fertilizers has been reported (Lugon-Moulin et al., 2006) but restricted to only 36 samples. More elaborate surveys, including a wide range of TEs, have been made for specific countries such 89 90 as Germany (Kratz et al., 2016), Spain (Otero et al., 2005), Chile (Molina et al., 2011) and Peru 91 (Bech et al., 2010). In 2008, Nziguheba and Smolders analyzed metals in 196 different 92 commercial mineral fertilizers sampled from 12 countries of the EU-15. The mean Cd concentration was 36 mg Cd kg⁻¹ P₂O₅. About 21% of the EU-15 samples contained more than 93 60 mg Cd kg⁻¹ P₂O₅, the current Cd limit in Europe. That survey was probably one of the largest 94 95 at that time to represent EU-15. A drawback of the sampling strategy was that the number of 96 samples was not proportional to the consumption of P_2O_5 in the countries from which it was 97 sampled. For example, 22% of the samples had been obtained from Ireland while the mineral P 98 consumption in that country was about 3% of the EU15 in 2011 (EUROSTAT, 2019). In that 99 respect, the frequency distribution of the samples was not an unbiased estimate.

100 Against this background, this study aimed to survey TE concentrations in mineral P fertilizers 101 consumed in EU-28+1 and to estimate a weighted average TE input in Europe, i.e., 102 concentrations relative by consumption. It is hypothesized that this consumption based 103 sampling strategy will provide a robust estimate of TE concentrations in mineral P fertilizers 104 that are commercially available in EU28+1, and that this estimate will differ from previous 105 estimates with more restricted or biased sample set. The chemical analyses were run with a 106 quality control program, to ensure the accuracy of the method used. Here, ICP-MS was used, 107 targeting 26 different elements, but reduced to 21 for which the analyses were then considered 108 reliable as shown below.

109 2. Materials and methods

111 Between January and June 2014, a total of 414 P fertilizer samples were collected. Small 112 samples (100 - 500 g each) were obtained from 25 European countries and Norway by 113 collaborators who supplied the samples on a voluntary basis (Table 1). The suppliers included 114 representatives from academia, industry, research station, colleagues in universities or 115 authorities. There were no samples from three EU-28 countries: Malta, Slovenia and Ireland. 116 Table 1 shows that the sample numbers were roughly in proportion to the total national 117 inorganic P consumption. The largest underrepresentation was from Italy followed by Poland 118 while samples from Romania and the UK are rather overrepresented. The samples from Poland 119 had different packages labelled with the same name and the mineral composition detected was 120 rather similar for samples with the same name (data not shown). Hence it is likely that these 22 121 samples represent only about 7 different products sampled in replicate.

122 The fertilizer samples included NPK's, phosphate rock samples, processed phosphates such as 123 monoammonium phosphate (MAP), diammonium phosphate (DAP), single super phosphate 124 (SSP) and triple super phosphate (TSP). Organic fertilizers or single N or K fertilizers were not 125 requested. The labelling suggested that there were 3 organic P fertilizers.

126 2.2. Sample preparation and analysis

127 Upon arrival, all samples were transferred to 100 mL plastic containers, closed and stored. 128 Subsamples were subsequently ground with a commercial coffee grinder (Moulinex). Five 129 pulses of 4 seconds grinding were given to about 6 - 7 g fertilizer. About 5 g of the ground 130 sample was then oven-dried at 40° C for at least 24 hours.

About 200 mg of each sample was weighed accurately on an analytical scale into a 10 mL (not
acid washed) glass digestion tube. One mL of ultrapure HNO₃ (Chem-Lab NV, nitric acid 65%
ultrapure) was added with a pipette, thereby rinsing down all particles adhering to the tube

134 walls. The tubes were allowed to stand overnight and subsequently heated, starting at a temperature of 90° for about 30 minutes and at 160° for 2 hours. Digestions were carried out in 135 136 a Gerhardt Kjeldatherm digestion block. This digestion was carried out per batch of maximum 137 88 samples, which included 2 replicates of each sample, 3 replicates of a reference sample and 138 3 blanks (except one batch that was analyzed with only 2 blanks). After digestion, the samples 139 were allowed to cool down and diluted to 10 ml with ultrapure (Milli-Q) water. The digestion 140 tubes were sealed properly with parafilm and homogenized. These samples were diluted 200-141 fold with ultrapure water prior to analysis. Procedural blanks and reference material were also 142 subjected to all these treatments.

143 All diluted samples were analyzed for 26 elements by Inductively Coupled Plasma Mass 144 Spectrometry (ICP-MS; Agilent 7700x). A mixture of scandium (Sc), iridium (Ir) and rhodium (Rh), prepared at about 30 μ g L⁻¹ (Inorganic Ventures) was used as internal standard. Details 145 146 for the method of analysis are given in Table A.1 of the Supplementary Data. The Limits of 147 Quantification (LOQ) of the ICP-MS are not given since the LOQs determined in the calibration 148 standard solution are lower than those in the procedural blanks. The LOQs were therefore only 149 based on the procedural blanks (pure acid digests, also 200 times diluted). These LOQs were calculated as 10 times the standard deviation of the procedural blanks (in μ g or mg L⁻¹) of each 150 batch and converted back to a solid basis in the fertilizer (ug kg⁻¹ or mg kg⁻¹) using the 151 152 liquid:solid ratio of the acid digests. The mean LOQ of the fertilizer analysis of the 12 batches 153 is given in Table 2, in addition to the descriptive statistics of the fertilizer composition. The 154 mean LOQ was highest (i.e. poorest detection) for Pb and two other elements that will not be 155 reported further (Ag and Si), when expressed relative to the mean concentration in the fertilizers 156 (data not shown). The LOQs for Pb varied among the 12 batches between $0.08 - 16 \text{ mg Pb kg}^{-1}$ 157 ¹, illustrating the Pb contamination of lab chemicals. The fraction of samples that had a 158 concentration below LOQ was highest for Pb and Sb and two other elements that will not be

reported further (Ag and Si). Trace elements were above the procedural quantification limit in
minimal 75% of the samples except for Pb (43%), for Sb (60%) and for three other elements
that will not be reported further (Ag, Se and Si). For Cd, the fraction of samples that were above
the LOQ was 75% (Table 2).

163 A preliminary experiment was set-up to identify potential contamination by grinding and to 164 quantify the reduction in variance among replicates due to grinding. This was done on a 165 standard granular mineral fertilizer collected from Ireland in 2005. Briefly, 3 replicates of about 166 1 g of the original granular sample were weighed in 100 mL digestion tubes, digested with 5 167 mL nitric acid and treated as described above. Finally, samples were diluted with ultrapure 168 water to yield the same liquid:solid ratio as the digests of the ground samples. The same granular 169 fertilizer was ground and analyzed in three replicates of 200 mg with 1 mL acid and finally 170 diluted to 10 mL, homogenized and further diluted 100-fold. The results of this preliminary 171 experiment showed that there were no significant changes in the composition between ground 172 and unground samples (data not shown), except for a markedly large effect on Mo (ground: 3.3 \pm 1.8 mg Mo kg⁻¹ versus unground: 1.2 \pm 0.5 mg Mo kg⁻¹, mean data with standard deviation 173 174 are presented, n = 3) and in B (data not shown, likely due to glassware contamination). It is 175 possible that some Mo from the grinding steel is contaminating the sample. However, that 176 difference in Mo ground versus non ground Mo is not statistically different and is mainly due 177 to one positive outlier, suggesting contamination. In addition, further analysis of the 414 fertilizer samples showed that a few of the ground samples had Mo <0.2 mg Mo kg⁻¹ illustrating 178 179 that the contamination may have decreased once a large number of samples were ground. For Cd, the mean Cd concentration in ground samples was 6.5 ± 0.6 mg Cd kg⁻¹ versus 7.2 ± 2.2 180 mg Cd kg⁻¹ in unground samples, i.e. not significantly different and illustrating higher variation 181 182 among the unground granular fertilizer replicates. In general, several analytes had higher

183 coefficient in variation among replicates (>30%) for the unground fertilizers and it was 184 concluded that grinding is required to reduce variance and that the contamination is minor.

185 2.3. Quality assurance and control

186 A certified reference sample was obtained from the Institute of Reference Materials and 187 Measurements (IRMM, Geel, Belgium) of the European Joint Research Institute. This reference 188 sample, BCR-032, is a Moroccan rock phosphate with i) certified values for CaO, P₂O₅, SiO₂, 189 SO₃, Al₂O₃, MgO, Fe₂O₃, ii) indicative values for As, B, Cd, Cr, Co, Cu, Hg, Mn, Ni, Ti, V, Zn 190 and iii) additional values for Na, K, Ag, Mo, Pb, Sb, Se, Th, U. These certified concentrations 191 were converted to an elemental concentration (e.g. CaO to Ca) and converted to a total fertilizer 192 weight basis, not per unit P₂O₅. The repeated analysis of the certified reference material (Table 193 3) showed that the analysis of the most important elements Cd, P and U were on average within 194 6% of the certified or indicative/additional values. For other elements, this was within 20% 195 except As (21%) and Na (26%) and 5 other elements that will not be reported further (B, Si, Ti, 196 Se and Ag). Boron had a high recovery due to contamination from the laboratory glassware, as 197 described above. Silicon and Ti had a low recovery due to the fact that these elements are not 198 acid soluble. Selenium recovery was low for unknown reasons. Selenium is traditionally a 199 difficult element to analyze on ICP-MS, often leading to an overestimation due to interferences. 200 Silver, finally, is difficult to detect in nitric acid solution in ICP-MS due to strong memory 201 effects. Since Ag is not relevant, we chose not to measure all samples in other matrices. The 202 reproducibility of the analyses was monitored using the Coefficient of Variation (CV) between 203 analytical replicates (n = 2). When the CV was more than 20% for Cd (n = 23), analysis was 204 repeated and the mean of all the replicates (n = 4) was used for the re-analyzed samples. In 205 total, the 414 samples were analyzed in 12 batches. The median CVs among replicate analysis 206 was lower than 10%, in most cases even lower than 5% (Table A.2 of the Supplementary Data).

207 The CVs logically increased for samples with lower TE concentrations. For Cd, the median CV208 was only 3%.

209 2.4. Data handling

When the mean of all analytical replicates was below LOQ, the value was changed into "nd" (not detectable) of the corresponding batch. For reporting descriptive statistics, these values were subsequently converted to the mean LOQ/2 of all batches and the number of such samples was recorded.

214 **3. Results and discussion**

215 3.1. Composition of mineral fertilizers

216 Table 2 gives the summary of the elemental composition of the 414 samples. The % P₂O₅ in 217 the samples ranged 3 - 60 %, mean 21%. The number of samples with % P₂O₅ <5% was 21 (=5 218 % of total sample number), suggesting that the majority of samples are indeed pure or blended 219 mineral P fertilizers. A few of the fertilizers contained unusually large concentrations of TEs, 220 probably added as micronutrient, this was not always clearly stated on the packages. Six samples contained $>500 \text{ mg Cu kg}^{-1}$ and were green or blue, 17 samples had $>1000 \text{ mg Zn kg}^{-1}$ 221 222 ¹. Table A.3 of the Supplementary Data presents the mean TE concentrations of the P fertilizers 223 collected in each country. The variation in TE concentrations in P fertilizers sold in the different countries was up to two orders of magnitude, e.g., the country mean Cd concentrations in the P 224 fertilizers ranged $0.16 - 12 \text{ mg Cd kg}^{-1}$ while for U this was $0.60 - 78 \text{ mg U kg}^{-1}$. However, this 225 226 does not imply a higher TE accumulation or higher risk in the countries where P fertilizers with 227 large TE concentrations are sold because accumulation depends, in addition to the inputs, on the natural background, soil pH and climate and the TE risks depend on the soil TE 228 229 bioavailability and crop selection among others.

230 The elemental correlation matrix revealed significant associations (Table A.4 of the 231 Supplementary Data). Correlations of TE with P concentration were strongest for Cd, U and V 232 followed by weaker correlations for Sb, Cr, Al, As and Ni (Table 4). The correlations with Cd 233 and U concentration are shown in Figure 1. These correlations suggest that the rock P is the 234 major source of these elements. For both elements, there was a strong segregation between low Cd/P_2O_5 ratio (lower than 5 mg Cd kg⁻¹ P₂O₅) and high Cd/P₂O₅ ratio. The same is true for the 235 236 U/P_2O_5 relationship (Figure 1). The data were split between these low (n = 126) and high (n = 126) 288) Cd containing P-fertilizers, using a threshold of 5 mg Cd kg⁻¹ P₂O₅. There were marked 237 and statistically significant lower TE concentrations (mg kg⁻¹ fertilizer) in the low Cd than in 238 239 high Cd containing fertilizers for U, V, Cr, Fe, Ni, As, Al and Sb whereas the reverse was true 240 for Mo, Mn and Cu (Table 4). No differences between low and high Cd containing fertilizers 241 were found for Pb, Zn and Co. This goes back to the well-known different rock-P sources in P 242 fertilizers, i.e., those derived from the more common, sedimentary rocks have high Cd and U 243 concentrations, those derived from the less common igneous rock-P have low Cd and U 244 concentrations, as recently shown by Kratz et al. (2016). That latter study analyzed 68 rock 245 phosphates and found similar trends in TE concentrations between the two types of rock 246 phosphates, i.e., higher concentrations in sedimentary than igneous rock phosphates for Sb, Cr, 247 Al, As, Ni, Be, Mo, Pb, V, Se, Tl, B and Zn, in addition to Cd and U, while the reverse was true 248 for Co, Cu, Sn, Mn, Ti, Fe, and Sr, except for Mo and Fe and for some TE for which in our 249 study, no significant differences were found. The strongest correlations were found among Cd, Cr, V and U (r > 0.75). The correlation between U and Cd is shown in Figure 2 and visual 250 251 evaluation suggest that there are two different groups of high Cd rock phosphate that differ in 252 U/Cd ratio. Possibly, this is also related to the origin of the rock phosphate, as the U/Cd ratio 253 of sedimentary rock phosphates was higher than the U/Cd ratio of igneous rock phosphates (i.e. 254 4 and 2 respectively) in the study of Kratz et al. (2016). In addition, this means that changing 255 from a high to a low Cd containing mineral P fertilizers does not automatically decrease the U 256 concentration of the fertilizer and vice versa. Interestingly, the former was observed in a study 257 by Schipper et al. (2011) in a long-term field trial in which the type of mineral fertilizer was 258 changed after the first 5 years, from a single superphosphate to a triple superphosphate, and in 259 which the soil Cd accumulation rate decreased after this change, while this decrease was not 260 observed in the soil U accumulation rate. However, differences in processing the rock 261 phosphates could also contribute to differences in TE concentrations. In our study, no 262 significant difference in Cd and U concentrations (on a P basis) was observed between SSP and 263 TSP fertilizers, however, there were significant differences between the superphosphate 264 fertilizers, the blended fertilizers (NP, PK and NPK fertilizers) and the ammonium P fertilizers, 265 with lowest Cd and U concentrations (on a P basis) generally found in the blended NPK fertilizers and in the monoammonium phosphate (MAP; Table A5 in the Supplementary Data). 266

267 3.2. The environmental relevance of the trace element concentrations in the mineral fertilizer

This study is probably first in obtaining a balanced survey of a large number of fertilizers and measuring different TEs with associated quality control and quality assurance. The collected data may serve risk assessment of TEs, and have meanwhile been used to better evaluate i) the Cd input in Europe (Smolders, 2017) and ii) the current Cd mass balance in EU countries, whereby the measured average national Cd concentrations in the P fertilizers from this study, the P consumption and local soil, climate and crop properties were taken into account (Römkens et al., 2019).

Fertilizer TE concentrations become environmentally relevant when fertilizer application becomes a significant source of TE in soil and when the TEs have a potential effect, either as a contaminant or as an essential nutrient. Only the first part will be addressed here by evaluating the TE concentration in the fertilizer to the background concentrations in soil. In Europe, TE concentrations in agricultural soils have been monitored with a grid based strategy, allowing an 280 unbiased estimate of average soil TE concentrations (Reimann et al., 2014). The P normalised 281 TE concentrations in the fertilizers were related to the average aqua regia soluble TE 282 concentrations of arable soils (Table 5) at an equal yearly application of mineral P fertilizer of 20 kg P ha⁻¹, which is at the higher end of the range of mineral P doses in EU (Six and Smolders, 283 284 2014). This estimate shows that the yearly potential TE accumulation via P application, relative 285 to the TE concentration in soil, is highest for U, followed by Cd and then by other TEs and this 286 corroborates the trends found in literature, i.e., due to the relative high concentrations in the 287 mineral fertilizers and the low concentrations in soils, U and Cd have the highest enrichment 288 potential. For example, for As or Pb this is a factor 30 to 65 respectively lower than for Cd. The 289 measured accumulation of U and Cd in soils in long-term field trials is however somewhat 290 contradictory, illustrating that local factors determine the final TE accumulation. For example, 291 in the long-term trials of Rothamsted Research was found that soil Cd concentrations increased 292 in grassland by a factor of 2.6 over about 100 years in P-fertilized plots compared to a factor of 293 1.5 in corresponding unfertilized plots (Jones et al., 1987; Rothbaum et al., 1986). In contrast, 100 years of P fertilization increased topsoil U levels with about 0.45 mg U kg⁻¹ soil relative to 294 a background concentration of about 2.4 mg U kg⁻¹ soil observed at the start (as measured in 295 296 archived soil) or relative to similar values measured in the no-P treatment, i.e. the U 297 concentrations only increased by a factor of 1.2 after about 100 years of P application 298 (Rothbaum et al., 1979). In contrast, in the study of Bigalke et al. (2017), the soil Cd increase 299 during about 30 years of mineral fertilizer use was minor (maximum a factor of 1.1 increase), 300 while soil U concentrations increased in four out of six experimental field trials, up to a factor 301 1.3, i.e., from ~1.7 to ~2.25 mg U kg⁻¹ in one of the field trials. Off course, soils with initially 302 low background TE concentrations will be more affected by mineral P fertilization. In addition, 303 most U data in soil, as in the Rothamsted Collection and in the Swiss study of Bigalke et al. 304 (2017), refer to real total concentrations (either based on radiochemical methods or HF

305 digestion). In our estimate, the aqua regia soluble U of EU in soil was used (mean 1.1 mg U kg⁻ ¹;Reimann et al., (2014)). By using the real total U concentrations in soils (2.6 mg U kg⁻¹; XRF 306 307 based; Reimann et al. (2014)), the order reversed and Cd input by mineral P fertilizers becomes 308 more important than U (0.113 % per year for U compared to 0.172 % per year for Cd). Finally, 309 the exposure based ranking in Table 5 needs to be put into a risk perspective further by including 310 all aspects of risks of TE in the environment, such as i) plant uptake and accumulation in the 311 food chain and ii) by estimating long-term accumulation by taking crop offtake and leaching 312 potential into account.

313 3.3. The cadmium concentrations in mineral P fertilizers

There were highly significant differences in mean Cd/P₂O₅ concentration ratios among countries, largest mean values were found in Portugal, Spain, Poland and UK and lowest values in Romania, Sweden, Finland and Estonia (Figure 3).

317 Selected comparisons of Cd/P₂O₅ ratios with earlier data collected in the EU are given in Table 6. The sample mean concentration was 28 mg Cd kg⁻¹ P₂O₅ while the corresponding value was 318 36 mg kg⁻¹ P_2O_5 in the earlier estimate of 2008. The percentage samples exceeding the current 319 Cd limit of 60 mg Cd kg⁻¹ P₂O₅ was 11%, while this was 21% in 2008. An EU-28+1 weighted 320 321 mean Cd concentration was estimated from national means and the national P consumption statistics, yielding 30 mg Cd kg⁻¹ P₂O₅, i.e., 17% lower than that used in the most recent EU-28 322 323 Cd mass balance (Six and Smolders, 2014). This value could be refined by other statistical tools 324 such as addition of older data from Ireland, Germany and France or randomly selecting data 325 from each country in proportion to the P use, however it is unlikely that different calculations 326 would change the weighted mean largely, as it is not very different from the samples mean.

327 **4. Conclusions**

328 The TE concentrations in mineral P fertilizers collected in EU28+Norway were significantly 329 correlated with the P concentrations for Cd, U, V, Sb, Cr, As and Ni, suggesting that these TEs 330 originate from the rock phosphate used. About 70% of the collected fertilizers had a high TE/P ratio, while the rest had a low TE/P ratio, suggesting that fertilizers sold in EU28+Norway are 331 332 based on two distinct P rock sources, likely of sedimentary or igneous origin. Potential increase 333 of TE concentrations, relative to their background concentrations, by application of mineral P fertilizers in EU28+Norway agricultural soils ranks U>Cd followed by others. In addition, the 334 335 U and Cd concentrations in the P fertilizers were strongly correlated, however two distinct U/Cd 336 ratio's, i.e. 2 and 10 (on a weight basis), were observed. Finally, the mineral fertilizers were 337 collected with a consumption based strategy, that allowed the calculation of a weighted mean concentration of 30 mg Cd kg⁻¹ P₂O₅. The collected data from this study can be used for risk 338 339 assessment of TEs in EU28+Norway agricultural soils, however additional aspects of risks 340 related to TEs should be included, such as TE plant uptake and food chain accumulation.

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- 343 Appendix A. Supplementary Data

344 **References**

345	Bech, Jaume, Suarez, M., Reverter, F., Tume, P., Sánchez, P., Bech, Joan, Lansac, A., 2010.
346	Selenium and other trace elements in phosphate rock of Bayovar-Sechura (Peru). J.
347	Geochemical Explor. 107, 136–145. https://doi.org/10.1016/j.gexplo.2009.08.004
348	Bigalke, M., Ulrich, A., Rehmus, A., Keller, A., 2017. Accumulation of cadmium and uranium
349	in arable soils in Switzerland. Environ. Pollut. 221, 85–93.
350	https://doi.org/10.1016/j.envpol.2016.11.035
351	EU, 2019. REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
352	laying down rules on the making available on the market of EU fertilising products and
353	amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing
354	Regulation (EC) No 2003/2003 [WWW Document]. URL https://eur-lex.europa.eu/legal-
355	content/EN/TXT/?uri=CELEX:32019R1009 (accessed 10.14.19).
356	EUROSTAT, 2019. Consumption of inorganic fertilizers_Phosphorus [WWW Document].
357	URL https://appsso.eurostat.ec.europa.eu/nui/submitViewTableAction.do (accessed
358	10.14.19).
359	Jiao, W., Chen, W., Chang, A.C., Page, A.L., 2012. Environmental risks of trace elements
360	associated with long-term phosphate fertilizers applications : A review. Environ. Pollut.
361	168, 44-53. https://doi.org/10.1016/j.envpol.2012.03.052
362	Jones, K.C., Symon, C.J., 1987. Retrospective analysis of an archived soil collection. I. Metals.

- 363 Sci. Total Environ. 61, 131–144.
- Jones, K.C., Symon, C.J., Johnston, A.E., 1987. Retrospective analysis of an archived soil
 collection II. Cadmium. Sci. Total Environ. 67, 75–89.
 https://doi.org/https://doi.org/10.1016/0048-9697(87)90067-2

- Juste, C., Tauzin, J., 1986. Evolution du contenu en métaux lourds d'un sol de limon maintenu
 en jachère nueaprès 56 années d'application continu de divers d'engrais et amendements.
 Comptes Rendus de l'Académie d'Agriculture Française 72, 739–746.
- Kratz, S., Schick, J., Schnug, E., 2016. Trace elements in rock phosphates and P containing
 mineral and organo-mineral fertilizers sold in Germany. Sci. Total Environ. 542, 1013–
- 372 1019. https://doi.org/10.1016/j.scitotenv.2015.08.046
- Lugon-Moulin, N., Ryan, L., Donini, P., Rossi, L., 2006. Cadmium content of phosphate
 fertilizers used for tobacco production. Agron. Sustain. Dev. 26, 151–155.
 https://doi.org/10.1051/agro
- McBride, M.B., Spiers, G., 2001. Trace element content of selected fertilizers and dairy
 manures as determined by ICP-MS. Commun. Soil Sci. Plant Anal. 32, 139–156.
 https://doi.org/10.1081/CSS-100102999
- McLaughlin, M.J., Tiller, K.G., Naidu, R., Stevens, D.P., 1996. Review: the behaviour and
 environmental impact of contaminants in fertilizers. Aust. J. Soil Res. 34, 1–54.
 https://doi.org/https://doi.org/10.1071/SR9960001
- Molina, M., Aburto, F., Calderón, R., Cazanga, M., Escudey, M., 2011. Trace Element
 Composition of Selected Fertilizers Used in Chile: Phosphorus Fertilizers as a Source of
 Long-Term Soil Contamination. Soil Sediment Contam. An Int. J. 18, 497–511.
 https://doi.org/10.1080/15320380902962320
- Nziguheba, G., Smolders, E., 2008. Inputs of trace elements in agricultural soils via phosphate
 fertilizers in European countries. Sci. Total Environ. 390, 53–57.
 https://doi.org/10.1016/j.scitotenv.2007.09.031
- 389 Otero, N., Vitòria, L., Soler, A., Canals, A., 2005. Fertiliser characterisation: Major, trace and

- 390 rare earth elements. Appl. Geochemistry 20, 1473–1488.
 391 https://doi.org/10.1016/j.apgeochem.2005.04.002
- 392 Reimann, C., Birke, M., Demetriades, A., Filzmoser, P., O'Connor, P., (editors), 2014.

Chemistry of Europe's Agricultural Soils, Part A Methodology and Interpretation of the

- 394 GEMAS Data Set. Geologisches Jahrbuch (Reihe B 102), Schweizerbarth, Hannover. 523.
- 395 Rogasik, J., Kratz, S., Funder, U., Panten, K., Barkusky, D., Baumecker, M., Gutser, R., Lausen,
- P., Scherer, H.W., Schmidt, L., Schnug, Ewald, 2008. Uranium in soils of German longterm fertilizer trials, in: Schnug, E., De Kok, L.J. (Eds.), Loads and Fate of FertilizerDerived Uranium. Backhuys Publishers, Leiden, pp. 135–166.
- 399 Römkens, P., Voogd, J.C., Kros, H., Rietra, R., Yoo, J., Louagie, G., Smolders, E., De Vries,
- W., 2019. A spatially explicit model to calculate Cadmium balances in agro- ecosystems
 in the EU-27: model description and scenario analysis. [WWW Document]. URL
 https://www.asktheeu.org/en/request/5352/response/17034/attach/6/Paper metal balances
 Europe final concept 14 11.pdf (accessed 10.14.19).
- 404 Rothbaum, H.P., Goguel, R.L., Johnston, A.E., Mattingly, G.E.G., 1986. Cadmium
- 405 accumulation in soils from long-continued applications of superphosphate. J. Soil Sci. 37,

406 99–107. https://doi.org/https://doi.org/10.1111/j.1365-2389.1986.tb00011.x

- 407 Rothbaum, H.P., McGavseston, D.A., Wall, T., Johnston, A.E., Mattingly, G.E.G., 1979.
 408 Uranium Accumulation in Soils From Long-Continued Applications of Superphosphate.
- 409 J. Soil Sci. 30, 147–153. https://doi.org/10.1111/j.1365-2389.1979.tb00972.x
- 410 Sauerbeck, D., 1992. Conditions controlling the bioavailability of trace elements and heavy
 411 metals derived from phosphate fertilizers in soils. Proc. Int. IMPHOS Conf. Phosphorus,
- 412 Life Environ. 419–448.

Schipper, L.A., Sparling, G.P., Fisk, L.M., Dodd, M.B., Power, I.L., Littler, R.A., 2011.
Agriculture, Ecosystems and Environment Rates of accumulation of cadmium and
uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer.
"Agriculture, Ecosyst. Environ. 144, 95–101. https://doi.org/10.1016/j.agee.2011.08.002

- 417 Six, L., Smolders, E., 2014. Future trends in soil cadmium concentration under current cadmium
 418 fluxes to European agricultural soils. Sci. Total Environ. 485–486, 319–328.
 419 https://doi.org/10.1016/j.scitotenv.2014.03.109
- Smolders, E., 2017. Scientific aspects underlying the regulatory framework in the area of
 fertilisers state of play and future reforms [WWW Document]. URL
 http://www.europarl.europa.eu/RegData/etudes/IDAN/2016/595354/IPOL_IDA(2016)59
 5354_EN.pdf (accessed 10.14.19).
- Tjell, J.C., Christensen, T.H., 1985. Evidence of increasing cadmium contents of agricultural
 soils, in: 5th International Conference on Heavy Metals in the Environment. Lekkas,
 T.D.L., Athens.
- 427 Ulrich, A.E., 2019. Cadmium governance in Europe's phosphate fertilizers: Not so fast? Sci.
 428 Total Environ. 650, 541–545. https://doi.org/10.1016/j.scitotenv.2018.09.014
- Wetterlind, J., Richer De Forges, A.C., Nicoullaud, B., Arrouays, D., 2012. Changes in uranium
 and thorium contents in topsoil after long-term phosphorus fertilizer application. Soil Use
- 431 Manag. 28, 101–107. https://doi.org/10.1111/j.1475-2743.2011.00376.x
- Williams, C.H., David, D.J., 1973. The effect of superphosphate on the cadmium content of
 soils and plants. Aust. J. Soil Res. 11, 43–56.

435 **Figure captions**

- 436 **Figure 1** Fertilizer Cd and U content increases with increasing P₂O₅ content of the fertilizer.
- 437 Data of all 414 European samples are shown and illustrating two major sources of P for
- 438 fertilizers, with high metals content (H: 60 mg Cd kg⁻¹ P_2O_5 and 400 mg U kg⁻¹ P_2O_5) or low
- 439 content (L, $<5 \text{ mg Cd kg}^{-1} P_2O_5$ and $<20 \text{ mg U kg}^{-1} P_2O_5$).
- 440 Figure 2 The association between U and Cd in the mineral fertilizers in Europe. The data
- 441 suggest that the P fertilizers are based on two different rock P sources groups with either U/Cd
- 442 ratio on a mass basis of about 10 or 2.
- 443 **Figure 3** The fertilizer Cd content (P₂O₅ unit based) per country, quantile plots show (in lines)
- 444 min-P25-P50-P75-max and outliers (points).

445 **Table captions**

446 Table 1 The number of samples and the fraction of total mineral P use of the EU28+Norway in
447 2017. Data of mineral P use are from EUROSTAT (2019).

Table 2 Descriptive statistics of the mineral P fertilizer composition of the 414 European
samples. Concentrations < the Limit of Quantification (LOQ) of each batch were converted to
the mean LOQ/2 of the 12 analytical batches.

Table 3 Quality assurance results the recovery of elements as % of certified (or indicative or additional) concentrations in a European reference material, i.e. Moroccan Rock P BCR032. This sample was analyzed in replicates in each batch (n = 36 in total), the mean % recovery, and its standard deviation, is given. The large variation of Pb is likely because of lab contamination.

Table 4 Average fertilizer trace elements composition (mg of the element kg⁻¹ fertilizer) of samples divided between high Cd and low Cd based on an arbitrary division of 5 mg Cd kg⁻¹ P_2O_5 , supposedly splitting between igneous rock P (low Cd) and sedimentary rock P (high Cd) as source of P in the P fertilizer. The Pearson's correlation coefficient (*r*) between % P_2O_5 and trace element concentrations for the entire group of 414 mineral fertilizers is shown.

Table 5 The relative importance of P fertilizer application on the mineral balance in soil. This is expressed as a relative dose, i.e. a dose of elements calculated from the average elemental composition of P fertilizer (P unit based) and an EU wide average annual P application of 20 kg P ha⁻¹ relative to the average aqua regia soluble elements in the plough layer (3000 ton soil ha⁻¹, 0 - 23 cm surface layer with density of 1.3 kg L⁻¹) of European arable agricultural soils (Reimann et al., 2014).

467 **Table 6** Descriptive statistics of the Cd concentration on a P_2O_5 basis (mg kg⁻¹ P_2O_5) in current 468 and a previous EU survey.