1   **Tracing anthropogenic thallium in soil using stable isotope**

2   **compositions**

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13   **ABSTRACT:** Thallium stable isotope data are used in this study, for the first

14   time, to apportion Tl contamination in soils. In the late 1970's, a cement plant

15   near Lengerich, Germany, emitted cement kiln dust (CKD) with high Tl

16   contents, due to co-combustion of Tl-enriched pyrite roasting waste. Locally

17   contaminated soil profiles were obtained down to 1 m depth and the samples are

18   in accord with a binary mixing relationship in a diagram of Tl isotope

19   compositions (expressed as ε^{205}Tl, the deviation of the ^{205}Tl/^{203}Tl ratio of a

20   sample from the NIST SRM 997 Tl isotope standard in parts per 10^4) versus

21   1/[Tl]. The inferred mixing endmembers are the geogenic background, as

22   defined by isotopically light soils at depth (ε^{205}Tl $\approx$ –4), and the Tl emissions,

23   which produce Tl-enriched topsoils with ε^{205}Tl as high as ±0. The latter

24   interpretation is supported by analyses of the CKD, which is also characterized

25   by ε^{205}Tl $\approx$ ±0, and the same ε^{205}Tl value was found for a pyrite from the deposit

that produced the co-combusted pyrite roasting waste. Additional measurements for samples from a locality in China, with outcrops of Tl sulphide mineralization and associated high natural Tl backgrounds, reveal significant isotope fractionation between soils (ε^{205}Tl $\approx$ +0.4) and locally grown green cabbage (ε^{205}Tl between –2.5 and –5.4). This demonstrates that biological isotope fractionation cannot explain the isotopically heavy Tl in the Lengerich topsoils and the latter are therefore clearly due to anthropogenic Tl emissions from cement processing. Our results thus establish that isotopic data can reinforce receptor modelling for the toxic trace metal Tl.

INTRODUCTION

Thallium (Tl) is a rare and dispersed metallic element with an average upper continental crust abundance of 0.75 mg kg^{-1}.[1] Thallium concentrations in natural soils are typically less than 0.2 mg kg^{-1}, but they can reach levels of up to 100 mg kg^{-1} and higher in contaminated sites.[2] Important contamination pathways for Tl are acid mine drainage to sediments and atmospheric emissions from pyrite roasting and coal combustion to soils.[3,4,5,6] Similar to its neighbouring elements in the periodic table (Hg, Cd and Pb), Tl has high acute and chronic toxicities to mammals.[7] Thallium can occur both in monovalent and trivalent binding forms, but monovalent Tl(I) dominates the speciation in the aquatic environment due to the high redox potential of the Tl(III)/Tl(I) couple (Eh = +1.28 V). A most important property for its biogeochemical cycling is that the Tl^{+} cation has a similar ionic radius to K^{+} which contributes to Tl bioaccumulation in the food chain.[8,9,10] High translocation factors (root-to-leaf

50   Tl content ratio) were found for common vegetables like onions (10) and

51   kohlrabi (19) in weakly contaminated soils, and up to 350 (kohlrabi) at strongly

52   contaminated sites.[11] This renders food chain pollution by Tl a particular risk.

53   For more than half a century, the stable isotope systems of elements such

54   as H, C, O and a few others have been applied to investigate natural

55   fractionation conditions (temperatures, biogeochemical reactions), to constrain

56   system mass balances, or as tracers in geochemical and environmental studies.

57   The development of new high-precision analytical methods (MC-ICP-MS;

58   multiple collector ICP-MS) now allows the resolution of even small variations

59   in the stable isotope compositions of trace elements in complex natural samples,

60   thereby enabling environmental assessment studies for elements such as Cr, Se,

61   and Cd.[12] The results of such studies show that isotopic data can be used to

62   reinforce trace toxic element receptor modelling, adding significant weight of

63   evidence.

64   Such environmental investigations are also possible for the element Tl,

65   which is comprised of two stable isotopes, ^{203}Tl and ^{205}Tl, that have abundances

66   of about 30% and 70%, respectively. Previous work has furthermore

67   demonstrated that Tl exhibits surprisingly large natural stable isotope variations,

68   with an overall terrestrial variability of about 3‰ for the ^{205}Tl/^{203}Tl isotope ratio

69   (Figure 1).[13,14,15,16,17,18,19,20,21,22,23,24,25] The processes responsible for the

70   relatively large observed Tl isotope effects are still debated, but are likely to

71   include mass-independent fractionations that are related to isotopic variation in

72   nuclear volume.[26,27] This study reports on the first successful use of Tl stable

73   isotope ratios to assess the sources and biogeochemical fractionations of both

74 geogenic and anthropogenic Tl enrichments in the pedosphere. At present,

75 virtually no information exists on Tl isotope fractionation by high-temperature

76 anthropogenic reactions and biogeochemical processes, such as adsorption in

77 and plant uptake from contaminated soils. The aim of this study was, therefore,

78 to contribute the first stable Tl isotope data for a soil contaminated by cement

79 plant emissions and investigate key factors, which may contribute to

80 post-depositional Tl isotope variability in the pedosphere.

81 **EXPERIMENTAL SECTION**

82 **Studied Areas.** *(i). Lengerich, Germany.* Thallium emissions from a cement

83 plant near Lengerich, Germany, occurred in the late 1970's. Details about the

84 number and duration of the emission events were never released and the factory

85 owner has denied any official responsibility up to now. In 1979, the effects on

86 vegetation (leaf necrosis) around the cement plant and symptoms of poisoning on

87 grazing animals (*Alopecia areata*) led to the suspicion that Tl deposition at levels

88 of up to 400 μg m^{-2} d^{-1} was the cause of the toxic effects.[28] The emissions from

89 the cement plant were suspected to have originated from Tl-bearing pyrite

90 roaster calcine, which was added to the ground limestone meal as an Fe

91 supplement, until this was stopped by the authorities in 1979.[29,30] The roaster

92 calcine, a waste product from pyrite roasting for the production of sulfuric acid,

93 was acquired from a chemical plant (Sachtleben AG, Duisburg, Germany) that

94 used pyrite concentrates from its own sedimentary-exhalative ("SEDEX") Zn-Pb

95 sulfide-barite deposit in the Devonian slate belt of the Rhenish Massif near

96 Meggen (Germany).[31] While the roaster calcine was no longer accessible for

97 analysis because the pyrite mine, and hence calcine production, was abandoned

98   in 1992, a pyrite sample representative for the mine was found in the mineral

99   collection of the University Mainz. A sample of bypass cement kiln dust was

100   obtained from a former employee who does not wish to disclose his name.

101   Brown-leached soil (*podzolic Cambisol*) core samples were collected in 2011 on

102   grassland sites within 3 km to the northeast, and hence downwind (given the

103   prevailing SW wind pattern) of the cement plant, using a hammer-head soil

104   probe (Eijkelkamp, Netherlands). The samples were dried overnight in an oven

105   at 60 °C, gently disaggregated to pass through a 2-mm sieve, and homogenized

106   in an agate ball mill to 80-mesh (<180 μm) powder.

107   *(ii). Lanmuchang, Guizhou Province, China.* Further samples studied are from

108   Lanmuchang (105°30′23″E, 25°31′28″N), a remote rural area in southwest

109   Guizhou Province, China, where the local residents exhibit symptoms associated

110   with chronic Tl poisoning.[32] These symptoms are induced by the Tl-rich sulfide

111   mineralization of the area, which is particularly susceptible to weathering and

112   dispersion where outcrops are in the hills and due to sporadic artisanal mining

113   activities.[33,34] The Tl mineralization is primarily associated with the Permian

114   Longtan and Changxing Formations, which are comprised of limestone, argillite,

115   and an intercalation of coal seams. The host rocks have mostly undergone

116   intensive hydrothermal alteration and weathering, associated with silicification,

117   decalcification, argillization, kaolinization, and baritization. All sulfide minerals

118   such as cinnabar, realgar, orpiment, arsenopyrite and pyrite are rich in Tl, and

119   the local deposits have a long mining history (>350 years) for mercury but have

120   been worked exclusively for Tl since the 1990s.[33,34]

121   The soil horizons in the Lanmuchang area are not well developed

122   (*Oxisol*). The soils mainly originate from the weathering of outcrops and they

123   accumulate naturally on the slight to moderately steep slopes within the

124   mineralized area, including in alluvial and colluvial deposits ("red clay"). The

125   soil mineralogy is mainly comprised of quartz, kaolinite, illite and goethite, with

126   Fe_2O_3 concentrations between 100 and 200 g kg^{-1}.[33] Analyzed were a stream

127   sediment, rhizospheric soil, and the root, stem and leaves from locally grown

128   green cabbage (*Brassica oleracea* L. var. *capitata* L.) prone to high

129   accumulation of Tl.[35] The soil and sediment were air-dried in the laboratory and

130   then sieved to <2 mm. The plant leaves were cleaned using de-ionized water to

131   exclude any Tl contamination by dust or soil particles, air-dried, and then

132   crushed to fragments capable of passing through a 60-mesh sieve.

133   **Thallium Concentration and Isotope Analyses**. The mineral acids used were

134   of Merck suprapure grade (Mainz University) or distilled (Imperial College);

135   Milli-Q water (with ≥ 18.2 MΩ cm) was used throughout. The exchangeable Tl

136   fraction of the Lengerich soils was obtained by extraction with aqueous 1 M

137   NH_4NO_3 according to the procedure of the German Soil Protection and

138   Contaminated Sites Ordinance (DIN 19730:1997; solid/extractant ratio 1:2.5, 24

139   h shaking, centrifugation and 0.45 μm membrane filtration). For total Tl analysis

140   of the Lengerich soil and cement dust samples, approximately 50 mg of powder

141   were digested with an HNO_3 – HF acid mixture (15 mL conc. HNO_3 + 5 mL

142   conc. HF) using a closed-vessel microwave technique (PerkinElmer Multiwave).

143   Aqua regia was used for the digestion of the pyrite. The Lanmuchang samples

144   were first digested in sealed Savillex Teflon beakers using HF – HNO_3 for soils,

145   and HNO_3 – HCl mixtures for plant samples, and then redissolved in 6 M HCl to

146   establish a clear solution. The Tl concentrations of the Lengerich samples were

determined by quadrupole ICP-MS (Agilent 7700 at the University of Mainz)

and quantified using matrix-matched standards. For the Lanmuchang samples,

the Tl measurements were performed at the State Key Laboratory of

Environmental Geochemistry in Guiyang, using separate aliquots of the sample

materials and following published protocols.[34, 36] Quality control was

established by analyses of the certified reference soil samples GSD-2, GSD-8,

and GSS-4 (Chinese loess soils).

The Tl isotope analyses were carried out at the Imperial College MAGIC

Laboratories using previously established methods.[37,38] Briefly, the HF – HNO_3

sample digests were evaporated to dryness and re-dissolved in 1 M HCl, to

which Milli-Q water saturated with Br_2 was added to assure oxidation of all Tl

to the trivalent state. Chemical separation of Tl(III) from the sample matrix was

then performed using AG1-X8 anion exchange resin in 1000 µL (first stage) and

100 µL (second stage) columns. The Tl isotope measurements utilized a Nu

Plasma HR MC-ICP-MS instrument operated in low-resolution mode, in

combination with an Aridus desolvation system for sample introduction. The

measured $^{205}Tl/^{203}Tl$ ratios were corrected for instrumental mass bias and drift

using a combination of (i) external normalization to the $^{208}Pb/^{206}Pb$ ratio of

admixed NIST SRM 981 Pb, and (ii) standard sample bracketing with

concentration matched solutions of NIST SRM 997 Tl + NIST SRM 981 Pb. All

Tl isotope data for samples are reported using a ε notation relative to the NIST

SRM 997 Tl reference material ($\varepsilon^{205}Tl_{NIST997} = 0$):

$$\varepsilon^{205}Tl_{Sample} = 10^4 \cdot \frac{^{205}Tl/^{203}Tl_{Sample} - {}^{205}Tl/^{203}Tl_{NIST997}}{^{205}Tl/^{203}Tl_{NIST997}} \qquad (1)$$

170   Based on replicate measurements of matching standard solutions, the samples

171   were assigned an uncertainty (2sd) of ±0.35 to ±0.55 ε (Table 1), such that one ε

172   unit corresponds to about 4sd. Most of the 20 samples were analysed multiple

173   times (n = 2 to 4), and deviations between individual results were consistently

174   ≤0.5 ε. Measurements of the Aldrich Tl reference material furthermore yielded a

175   mean value of $\varepsilon^{205}Tl$ = –0.91 ± 0.35 (n = 2), in good agreement with the

176   reference data ($\varepsilon^{205}Tl$ = –0.81 ± 0.33).[39]

177   **RESULTS AND DISCUSSION**

178   The analysed soil profiles from Lengerich show the highest total and

179   NH_4NO_3-exchangeable Tl concentrations at the surface (0-10 cm), exponentially

180   decreasing with increasing depth (Table 1, Figure 2). These 'addition profiles'

181   indicate that the high Tl concentrations found in the topsoil horizon are not due

182   to accumulation during weathering of the parent rock, but are a consequence of

183   absolute non-pedogenic Tl gains.[40] This topsoil gain is most likely caused by

184   atmospheric emissions from the nearby cement plant, a hypothesis that is

185   corroborated by the prevailing wind direction and the larger absolute Tl gains

186   for soil profiles that were collected closer to the cement plant (Figure 2). In the

187   deepest soil samples (90-100 cm), representing the primary C horizon of

188   moraine glacial till mainly composed of marl, the total Tl concentrations of

189   about 0.1 mg kg^{-1} are considered to be characteristic of the local geogenic

190   background. This conclusion is supported by the observation that the relatively

191   mild 1 M NH_4NO_3 extractant, which is used to leach the exchangeable fraction

192   of elements, recovered only ≤2% of the total Tl budget for soil horizons deeper

193   than 40 cm (with total [Tl] <0.3 mg kg^{-1}), a value that is typical for

194   uncontaminated soils.[41] The exchangeable Tl fraction increases to up to 17% (of

195   total Tl) in topsoils from near the cement plant, suggesting that a highly mobile

196   form of Tl was added to the soils (Table 1). The observed rise in the

197   concentration of readily exchangeable Tl cannot, however, account for the

198   overall increase of the total Tl content (compare Figs. 2a and 2b). This indicates

199   some post-depositional loss in the mobility of the added anthropogenic Tl.

200   Further support for the proposed origin of the Tl enrichments in the

201   topsoils is provided by the Tl isotope compositions. A plot of $\varepsilon^{205}Tl$ against

202   1/[total Tl] displays an inverse linear relationship ($r^2 = 0.82$), indicative of

203   binary mixing between two different Tl pools (Figure 3). The Tl in the soils is

204   thereby a mixture between a reservoir with high Tl concentrations (1/[Tl] $\to$ 0;

205   [Tl] > 2 mg kg^{-1}) and a relatively heavy isotope composition ($\varepsilon^{205}Tl > -1$), and a

206   second pool representing the geogenic background, characterized by low Tl

207   contents (4 kg mg^{-1} < 1/[Tl] < 8 kg mg^{-1}; [Tl] $\approx$ 0.1 to 0.2 mg kg^{-1}) and light

208   isotope compositions ($\varepsilon^{205}Tl < -3.0$). Importantly, the inferred $\varepsilon^{205}Tl$ values of

209   the two endmembers are significantly different at the 99.9% confidence level.

210   The origin of the light Tl isotope composition of the geogenic background at

211   Lengerich, as recorded in the deepest soil profiles samples with $\varepsilon^{205}Tl \approx -4$, is

212   uncertain, particularly because average upper continental crust has a heavier

213   isotope composition of $\varepsilon^{205}Tl \approx -2$ (Figure 1). A possible explanation is that the

214   light isotopic signature of the marl is derived primarily from calcareous parent

215   material, as this may feature a seawater-derived isotopic signature similar to

216   modern seawater characterized by $\varepsilon^{205}Tl \approx -6$ (Figure 1).

217   An $\varepsilon^{205}Tl$ value of -0.36 ± 0.55 was measured for the Meggen pyrite,

218 which is enriched in Tl at 200 mg kg^{-1} (Fig. 3, Table 1). From the literature, it is

219 known that the fluidized bed furnace temperatures during pyrite roasting

220 (typically ~850 °C) are not high enough to achieve significant volatilization of

221 Tl (boiling point of Tl$_2$O is 1080 °C). The roasting calcines therefore still

222 contain Tl that is bound to the residual Fe oxides,[42] and at concentrations that

223 are three orders of magnitude higher compared to the sedimentary rocks, which

224 are commonly used as rawmix in cement production (commonly <0.5 mg

225 kg^{-1}).[43] The cement kiln dust (CKD) was found to have a Tl content of 66 mg

226 kg^{-1} and an isotope composition (ε^{205}Tl = –0.19 ± 0.40) that is identical, within

227 uncertainty, to the Meggen pyrite (Fig. 3, Table 1), which characterizes the most

228 likely mineral source of the Tl-enriched Fe oxide calcines that were added to the

229 rawmix.

230   The CKD typically has high Tl contents because the volatilized element

231 recirculates due to continuous return of the dust via the gas-suspension

232 preheaters, which gradually heat the rawmix by contact with the hot

233 dust-bearing gas stream from the rear of the rotary kiln. The recirculation

234 involves evaporation of Tl compounds in the rotary kiln, a process that is

235 supported (as with Pb) by the formation of volatile Tl(I) chloride species (TlCl

236 boiling temperature is 806 °C). Owing to the large surface area available, the Tl

237 compounds that were volatilized in the kiln condense onto the dust particles in

238 the preheaters.[43] Up to over 75% of the Tl from the rawmix (with commonly

239 <0.6 mg kg^{-1} Tl if uncontaminated) is thereby repartitioned onto the electrostatic

240 precipitator dust under normal process conditions.[43] A Tl accumulation cycle is

241 therefore formed between the kiln, the preheaters for rawmix drying, and the

242 exhaust gas purification system, from where the CKD is fed back into the

243   rawmix. Thallium is thus enriched in the CKD to a certain level, which is

244   generally limited by bypass purging at the kiln inlet to prevent build-up of

245   excess chloride salts in the cyclone preheaters. Such purging is preferably

246   performed at Tl concentrations of < 100 mg kg^{-1}, to enable waste disposal at

247   moderate costs.[43] Thirty years ago, such short bypass purging ("alkali bleed")

248   was often not coupled to an additional air pollution control device equipped with

249   electrostatic precipitators, as is nowadays the rule at cement works. In the past,

250   this may have hence led to short but intense blow-out events of Tl-enriched

251   CKD. The Tl compounds that were condensed on the surfaces of dust particles

252   and emitted during bypass processing, were highly mobile, as leaching of the

253   dust with NH_4NO_3 releases 80% (Table 1), and with EDTA solutions even

254   nearly 100% of the Tl budget.[44]

255   Particulate atmospheric emissions of Cd from high temperature

256   processes were found to be isotopically light relative to the source material,[45,46]

257   but no such fractionation was found here for Tl processed in a cement plant.

258   This is likely due to the pyroprocessing stage of cement manufacture, which

259   involves temperatures of up to 1450 °C in the kiln bed, and up to 2000 °C in the

260   firing zone, and is therefore expected to induce quantitative evaporation of the

261   Tl from the rawmix.[43] In fact, considering the 2sd uncertainties, the ε^{205}Tl value

262   of the CKD (–0.19 ± 0.40) is identical to that of the topsoil sample from Profile

263   2, which features the highest Tl concentration (3.2 mg kg^{-1}) and ε^{205}Tl = –0.08 ±

264   0.35 (Fig. 3, Table 1). These results reinforce our earlier conclusion that the

265   elevated Tl contents of the Lengerich topsoils are caused by Tl emissions from

266   the cement works. Since contamination ceased more than 30 years ago, it is

267   important to consider possible post-depositional changes in the isotope signature

268 of the contaminant due to biogeochemical processes in soils. As no constraints

269 are available in the current literature, we addressed this topic through isotopic

270 analyses of additional samples from the Lanmuchang site in China, which

271 features also high natural Tl enrichments albeit by natural processes of

272 pedogenic origin.

273 At Lanmuchang, the arable soil have Tl isotope compositions that are

274 somewhat heavier (with ε^{205}Tl ≈ +0.45) compared to the German soils (Table 1)

275 and common Chinese loess soils (Figure 1). While the Lengerich soils have

276 relatively low Fe+Mn concentrations (<1 wt.-%, with no enrichment in topsoil

277 horizon), the Lanmuchang soil features high Fe+Mn contents of >10 wt.-%

278 (*Oxisol*).[34] The isotopically heavier Tl of the latter soils may thus reflect

279 oxidation of Tl(I) derived from weathering of the local sulphide mineralization,

280 and subsequent scavenging of the thus formed Tl(III) by Fe-Mn oxyhydroxide

281 phases.[47] This hypothesis is backed up by (i) experimental studies which show

282 that adsorption of dissolved Tl(I) onto Mn oxides leads to an enrichment of

283 isotopically heavy Tl in the solid phase,[48] and (ii) findings that in marine and

284 riverine environments, the Tl bound to Fe-Mn oxides is almost universally

285 enriched in ^{205}Tl relative to dissolved and silicate-bound Tl (Figure 1).

286 Clearly, the enrichment of Tl in vegetables is generally related to high Tl

287 concentrations in rhizospheric soils, but the mobility of Tl is also affected by the

288 water and organic matter content, pH, mineralogy, and cation exchange capacity

289 of the soils. Moreover, speciation may be a key factor controlling Tl mobility.

290 Unfortunately, the Tl partitioning in the Lanmuchang soils has not yet been

291 measured, though it is known that the rate of Tl uptake by vegetables varies with

the partitioning of Tl in contaminated soils. The maximum uptake rate was observed for plants grown on soil containing Tl-bearing clay minerals, whilst soil enriched in Tl-bearing Mn oxides was found to have the lowest potential for Tl release and phytoaccumulation.[49,50] Nonetheless, a high bioaccumulation of Tl was observed for the Lanmuchang green cabbage leaves that were grown on the local soils, with a Tl concentration of more than 100 mg kg^{-1} (Table 1).

At Lanmuchang, the plants are expected to take up isotopically light Tl from the soils because only Tl(I) is bioaccessible, whilst the inaccessible Tl(III) is bound to soil oxides which are enriched in heavier ^{205}Tl. Indeed, our Tl isotope analyses reveal a significant fractionation of about –5 ε between young edible plant leaves and the soil (Table 1). The distribution of Tl concentrations in the green cabbage exhibits a systematic pattern, with young leaves ≈ old leaves > stems > roots. The isotopic data collected for the samples (Table 1) suggest that lighter Tl is not only enriched at the soil-root interface but that further isotope fractionation occurs along the physiologically controlled translocation pathway. This follows from the observation that the increasing enrichment of Tl within the green cabbage plant is accompanied by enhanced isotope fractionation, whereby the ε^{205}Tl values decrease from the cabbage root (–2.54) and the stem (–2.91) to the old leaves (–3.68) and young edible leaves (–5.39; Table 1). Whilst these limited data suggest an active enrichment of isotopically light Tl in the plant, they do not yet allow elucidation of the mechanisms responsible for the isotopic effects. However, the results are also important because they clearly demonstrate that the Tl isotope trends of the Lengerich soil profiles are not due to biogeochemical fractionations or the input of organic matter enriched in lighter Tl. Importantly, the latter processes would

317 generate isotopic trends in the opposite direction of the observed systematics.

318 **Environmental Implications**. As cement demand and production

319 continue to grow worldwide, and in particular in Asia with economic rise and

320 increasing construction activities, the contribution of cement plants to the

321 overall atmospheric emission inventory will become an important environmental

322 issue. This rise is, furthermore, accompanied, by a huge increase in the amount

323 of bypass CKD generated which cannot be recycled but must be disposed. In

324 1990, the US cement industry generated an estimated 12.7 million metric tonnes

325 of CKD from 111 plants in 38 states, and 4 million metric tonnes of this was

326 disposed in piles, quarries, and landfills.[51] Clearly, the co-combustion option

327 offered by cement kilns is thriving and playing an increasingly important role in

328 solid waste management.[52,53,54] As a consequence of the Lengerich pollution

329 case well known in that community, Tl concentration has become an emission

330 parameter pursuant to ambient pollution legislation. Hence, the use of solid

331 waste containing in excess of 2 mg kg^{-1} Tl was restricted by regulations in

332 Germany and other countries. Nowadays, low flue gas Tl emissions are achieved

333 if cement kilns meet the emission regulation standards and regular Tl emissions

334 of less than 10 kg a^{-1} were reported for 44 modern rotary and precalciner kiln

335 works in Germany in 2008.[55] However, such beneficial process conditions are

336 easily disturbed if the cement rawmix is contaminated by Tl-enriched waste

337 products or secondary kiln fuels. A severe pollution risk may then be posed by

338 Tl contamination and accumulation in the food chain, for example if vegetable

339 crops are grown in the neighbourhood of cement works. When crops from

340 contaminated sites are eaten, this may readily lead to Tl intake levels, which

341 exceeds the suggested WHO threshold value of 5 μg Tl d^{-1}.[56]

342   Our findings demonstrate that the historical emission of Tl-enriched dust

343   from the Lengerich cement plant can unequivocally be traced by the anomalous

344   Tl isotope compositions of the local topsoils. In fact, the source isotopic

345   signature is still well preserved, such that it can be linked to the original

346   emission events, even 30 years after deposition. However, this may be a

347   favorable exception rather than the rule. For example, it is conceivable that

348   continued deposition of plant debris, and organic material derived by

349   degradation thereof, may produce a gradual shift in the Tl isotope signature of

350   mature topsoils, i.e. toward lower ε^{205}Tl values in the A horizon. Such a shift,

351   however, is clearly not in accord with the Lengerich soil profiles, as these

352   feature relatively high ε^{205}Tl near the surface and lighter Tl isotope compositions

353   at depth. The Lanmuchang data suggest also that the Tl isotope characteristics of

354   anthropogenic emissions are less likely to be preserved in Fe-Mn-rich soils. In

355   particular, the Tl(I) species deposited by air pollution may be transformed

356   abiotically to less mobile Tl(III) by the ferromanganese oxide minerals which, in

357   turn, can generate significant post-depositional Tl isotope fractionations. Such

358   post-depositional processes may thus hamper the use of Tl isotope 'fingerprints'

359   for apportioning contamination sources. Hence, it will be necessary to further

360   study and clarify the role of pedospheric processes that can alter Tl isotopic

361   compositions until source apportionments, which are based on such records, can

362   be carried out with confidence. A more sophisticated approach such as Tl

363   isotope analysis in sequential soil extractions may then help to differentiate

364   pedogenic from anthropogenic fractionation patterns. In summary, the results of

365   the cases studies presented here provide an improved but still rudimentary

366   understanding of Tl cycling and isotope fractionation in both natural and

367 anthropogenic environments. In particular, further investigations are warranted

368 to elucidate the mechanisms of the significant Tl isotope fractionation by crops

369 that are known bioaccumulators of this toxic element.

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375 The authors declare no competing financial interest.

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Table 1. Total and NH_4NO_3-extractable Tl concentrations, and $\varepsilon^{205}Tl$ values in total digestions of the Lengerich and Lanmuchang samples. The Tl concentrations are for dried samples. All quoted uncertainties are 2sd. For the Tl concentrations, the uncertainties are based on triplicate sample analyses. For the $\varepsilon^{205}Tl$ values, 2sd was determined from multiple analyses of matching standard solutions and multiple ($n = 2 - 4$) analyses of samples (if not otherwise stated).

Sample	Total Tl (mg kg^{-1})	NH_4NO_3-extractable Tl (mg kg^{-1})	$\varepsilon^{205}Tl$ in total HF-HNO$_3$ digestions
Meggen pyrite	200 ± 15	-	–0.36 ± 0.55
Cement kiln dust	66 ± 5	54 ± 5	–0.19 ± 0.40
Soil Profile 1			
0-10 cm	3.17 ± 0.43	0.554 ± 0.045	–0.08 ± 0.35
10-30 cm	0.72 ± 0.08	0.086 ± 0.010	–1.56 ± 0.35
30-40 cm *	0.23 ± 0.02	0.020 ± 0.002	–2.55 ± 0.40
Soil Profile 2			

0-10 cm *	2.27 ± 0.18	0.243 ± 0.014	–0.88 ± 0.40
10-30 cm *	1.64 ± 0.29	0.150 ± 0.012	–1.69 ± 0.40
30-50 cm	0.63 ± 0.03	0.074 ± 0.004	–2.31 ± 0.35
50-90 cm	0.21 ± 0.04	0.007 ± 0.002	–3.59 ± 0.35
90-100 cm	0.15 ± 0.02	<0.001	–3.61 ± 0.35
Soil Profile 3			
0-10 cm	0.92 ± 0.06	0.063 ± 0.006	–2.00 ± 0.40
10-30 cm *	0.46 ± 0.02	0.021 ± 0.003	–2.59 ± 0.35
30-40 cm	0.16 ± 0.01	0.006 ± 0.001	–4.17 ± 0.40
Lanmuchong samples			
Stream sediment (SD05)	30	-	0.44 ± 0.35
Arable soil (S621)	30	-	0.45 ± 0.35
Green cabbage root	25	-	–2.54 ± 0.35
Green cabbage stem	83	-	–2.91 ± 0.35
Green cabbage old leaf	100	-	–3.68 ± 0.35
Green cabbage – young leaf (edible part)	105	-	–5.39 ± 0.35

* Sample analyzed only once.

Figure Captions

Figure 1. Overview of natural Tl isotope variations (shown as ε^{205}Tl values) found in various terrestrial reservoirs and meteorites. The hashed line at ε^{205}Tl $= –2$ denotes the inferred Tl isotope composition of the continental crust and the Earth's mantle. These are currently best defined by the data for loess and fresh mid-ocean ridge basalts, respectively (data compiled from refs. *13-25*).

Figure 2. Soil profiles of (a) 1 M NH_4NO_3-extractable Tl concentrations and (b) total Tl concentrations for the three grassland sampling sites near the Lengerich cement

plant. The site/soil profile numbers increase with increasing distance to the cement plant. Trend lines were drawn to guide the eye.

Figure 3. Plot of ε^{205}Tl vs. 1/total Tl for the HF – HNO_3-digested soil samples. Also shown are results for the Meggen pyrite and Lengerich cement kiln dust (CKD). The linear trend and associated R^2 value were calculated from the soil data only.

Typical Uncertainty
± 2sd

Hydrogenetic Fe-Mn crusts

Diagenetic Fe-Mn nodules

Deep-sea clays & oozes

Marine sulfides

Seawater

Rivers

Loess

Island arc lavas

Continental igneous rocks & mineralization

Ocean island basalts

Fresh mid-ocean ridge basalts

Black-smoker fluids

Altered ocean crust

←— -20   Meteorites   +30 —→

-14   -10   -6   -2   +2   +6   +10   +14

$\varepsilon^{205}Tl$