

1 Influence of environmental and anthropogenic parameters on thallium
2 oxidation state in natural waters

3

4 **Beatrice Campanella^{1*}, Alessandro D'Ulivo¹, Lisa Ghezzi², Massimo Onor¹, Riccardo Petrini²,**
5 **Emilia Bramanti¹**

6

7 ¹ Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici, via G.Moruzzi,
8 56124 Pisa, Italy

9 ² Università di Pisa, Dipartimento di Scienze della Terra, via S. Maria, 56126 Pisa, Italy

10

11 ***Corresponding author:**

12 E-mail: beatrice.campanella@pi.iccom.cnr.it

13

14

15 **ABSTRACT**

16 The abandoned mining area of Valdicastello Carducci (Tuscany, Italy) is characterized by the
17 massive presence of thallium in the acid mine drainages and in the valley stream crossing the
18 region. We previously found that Tl(III), generally considered the less stable oxidation state of
19 thallium, is present both in the stream and in tap water distributed in the area, whereas acid mine
20 drainages only contain Tl(I). These findings posed some concern related to the reactivity and
21 dispersion of this toxic element in the environment. Since the valence state of thallium determines
22 its toxicity, distribution and mobility, the study of thallium redox speciation appears crucial to
23 understand its environmental behaviour.

24 In this work, water samples collected from the mine drainages and the contaminated stream were
25 adopted as model to study the distribution of aqueous Tl(I)/Tl(III) as a function of light exposure
26 and solution properties and composition. The influence of three light sources and organic acids was

27 evaluated. Thallium speciation was also assessed in tap water after treatment with common
28 oxidizing agents, and in the rust crust collected from the public waterworks.

29

30 **Keywords**

31 Thallium; Tl-bearing pyrite; Natural waters; AMD; Photochemistry; Oxidation.

32

33

34

35 **1. Introduction**

36 In the last decades, thallium has become a ‘technology-critical element’ in our modern economy for
37 its increasing uses in new technologies. Because the solubility, mobility, bioavailability, and
38 toxicity of thallium depend on its oxidation state (Lan and Lin, 2005; Lin and Nriagu, 1999; Ralph
39 and Twiss, 2002; Xiong, 2009), studies of thallium speciation and transformations among species
40 are essential to understand its behavior in the environment. Thallium has been included by the U.S.
41 Environmental Protection Agency in the list of priority toxic pollutants (Cyjetko et al., 2010). More
42 than 285 papers contain information of Tl distribution in natural waters, soils, sediments and air
43 particulates, but only few among them present studies on speciation (Belzile and Chen, 2017).

44 Thallium has two principal oxidation states, Tl(I) and Tl(III), both of which are considered highly
45 toxic to living organisms: Tl(I) salts are very soluble and Tl^+ is similar to potassium, so it is able to
46 replace the latter during enzymatic reactions. Tl^{3+} induces an oxidative stress status in human cells
47 and it was found to be considerably more toxic than Tl^+ to the unicellular alga *Chlorella* (Molina et
48 al., 2017; Osorio-Rico et al., 2017; Rickwood et al., 2015). Thallium(I) is expected to be the
49 dominant species in aqueous solutions in equilibrium with atmospheric oxygen and in the absence
50 of complexing agents (Lin and Nriagu, 1999). From a thermodynamic point of view, conversion of
51 Tl(I) to Tl(III) would be expected only in the presence of extremely strong oxidants, such as MnO_4^-
52 or Cl_2 , and high alkalinity (Kaplan and Mattigod, 1998).

53 A severe thallium contamination has been recently discovered in the acid mine drainages (AMDs)
54 outflowing from tunnels in a past-mining area in the southern sector of the Apuan Alps (northern
55 Tuscany, Italy) (Campanella et al., 2016). In the abandoned mining sites, bacteria-mediated
56 oxidation of thallium-rich pyrite ores caused the production of iron(III) and hydrogen ions that
57 catalytically dissolved pyrite, thereby increasing the metal load in the AMDs. The Baccatoio stream
58 receives AMDs and crosses the Valdicastello Carducci village and the Versilia Plain, a densely
59 populated area. Thallium contamination also affects waters from a spring outflowing in the
60 Baccatoio catchment and until recently used for drinking water supply, so that this element became
61 widespread into pipeline encrustations (Campanella et al., 2016; D’Orazio et al., 2017; Perotti et al.,
62 2017). The content of thallium ranged from 0.05 to 1 $\mu\text{g/L}$ in potable water from public fountain,
63 from 0.7 to 48 $\mu\text{g/L}$ in tap water from private houses, from 10 to 130 $\mu\text{g/L}$ in the water of
64 Baccatoio, and from 300 to 800 $\mu\text{g/L}$ in AMDs (Campanella et al., 2017, 2016).

65 In a previous work (Campanella et al., 2017), we found by IC-ICP-MS analysis that only Tl(I)
66 characterizes the AMDs, which is in agreement with the host of Tl(I) in the Tl-bearing pyrite. On
67 the other hand, Tl(III) was present in notable amounts both in the superficial water of the Baccatoio
68 stream, where the AMDs converge, and in the tap water distributed in inhabited area. After these
69 findings, two main questions persisted: (i) how Tl(I) from AMDs oxidises to Tl(III) in the stream
70 water and (ii) why considerable amounts of Tl(I) and Tl(III) were detected in the tap water from
71 private houses? It appears that two different sources of Tl(III) are present in this complex system,
72 related to two independent mechanism of Tl(I) oxidation.

73 Metals oxidation cycles in natural waters are often mediated by photochemical processes (Allen et
74 al., 1996; Zafiriou et al., 1984). Some authors observed that the oxidation of Tl(I) in aqueous
75 solutions can take place during UV or sunlight irradiation (Karlsson et al., 2006; Li et al., 2005),
76 thanks to the production of possible oxidative species such as hydrogen peroxide or $\cdot\text{OH}$ (Paul,
77 2001). Especially the highly reactive transient hydroxyl radicals might represent strong oxidants,
78 considering that the production of hydroxyl radicals is speeded up by Fe(II) generated by

79 photoreduction (photo-Fenton reactions). Indeed, AMDs in the Baccatoio mining area are
80 characterized by high iron and manganese content, whose hydro-geochemistry is well known to be
81 able to influence the oxidation state of thallium (Davies et al., 2016; Gadde and Laitinen, 1974;
82 Huangfu et al., 2015; Peacock and Moon, 2012). The ability of Mn(IV) to oxidize Tl(I) is known
83 (Huangfu et al., 2015), while no spontaneous oxidation of Tl(I) from Fe(III) is expected on
84 thermodynamic grounds. In the case of iron, therefore, the combination with more chemical agents
85 and radiation might be fundamental to explain oxidation reactions otherwise not spontaneous in
86 natural systems.

87 Here we report the effect of natural and artificial radiation and of some chemical compounds on the
88 speciation of thallium in the contaminated waters. The knowledge of the redox speciation of
89 thallium in such systems is important in assessing the fate and transport of this toxic element
90 through the aqueous routes, and in the choice of appropriate remediation techniques.

91

92

93 **2. Materials and methods**

94 *2.1 Reagents*

95 High purity water (18.2 MΩ·cm) was obtained with an Elga Purelab-UV system (Veolia
96 Environment, Paris, France). TraceCERT® nitric acid (HNO₃, 69%), sulphuric acid (H₂SO₄, ACS
97 reagent 95-98%) iridium (analytical standard, 1000 mg/L Ir in 10 wt. % HCl), ammonium nitrate
98 (NH₄NO₃ 99.999% trace metals basis), diethylenetriaminepentaacetic acid (DTPA), hydrogen
99 peroxide (H₂O₂, 30%), acetic acid, sodium hypochlorite (NaClO, available chlorine 10-15%),
100 ammonium fluoride (NH₄F), and manganese(IV) oxide (MnO₂ 50 wt.% on activated carbon) were
101 purchased from Sigma-Aldrich. Arsenic(V) standard solution and ammonium iron(III) sulphate salt
102 were purchased from Carlo Erba (Italy). Standard solutions of Tl(I) were prepared by dilution of
103 1000 mg/L Tl in 0.5 mmol/L HNO₃ (Merck) in the eluent phase. Standard solution of Tl(III) was
104 prepared dissolving Tl(NO₃)₃·3H₂O (Sigma-Aldrich) in 5 mmol/L HNO₃ – 5 mmol/L DTPA. For

105 colorimetry of iron(II), 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ, $\geq 98\%$) obtained from Sigma-Aldrich
106 was used as the complexing reagent. PTFE filters (4 mm thickness and 0.20 μm pore diameter,
107 Sigma Aldrich) were chosen for the filtration.

108

109 2.2. Valdicastello Carducci and mining district

110 Figure 1 shows the area object of the study, located in the northwest of Tuscany (Italy).

111 Valdicastello Carducci is a small village having about 1000 inhabitants. From the end of the World

112 War II to 1990 an intense mining activity characterized the mountainous area immediately north of

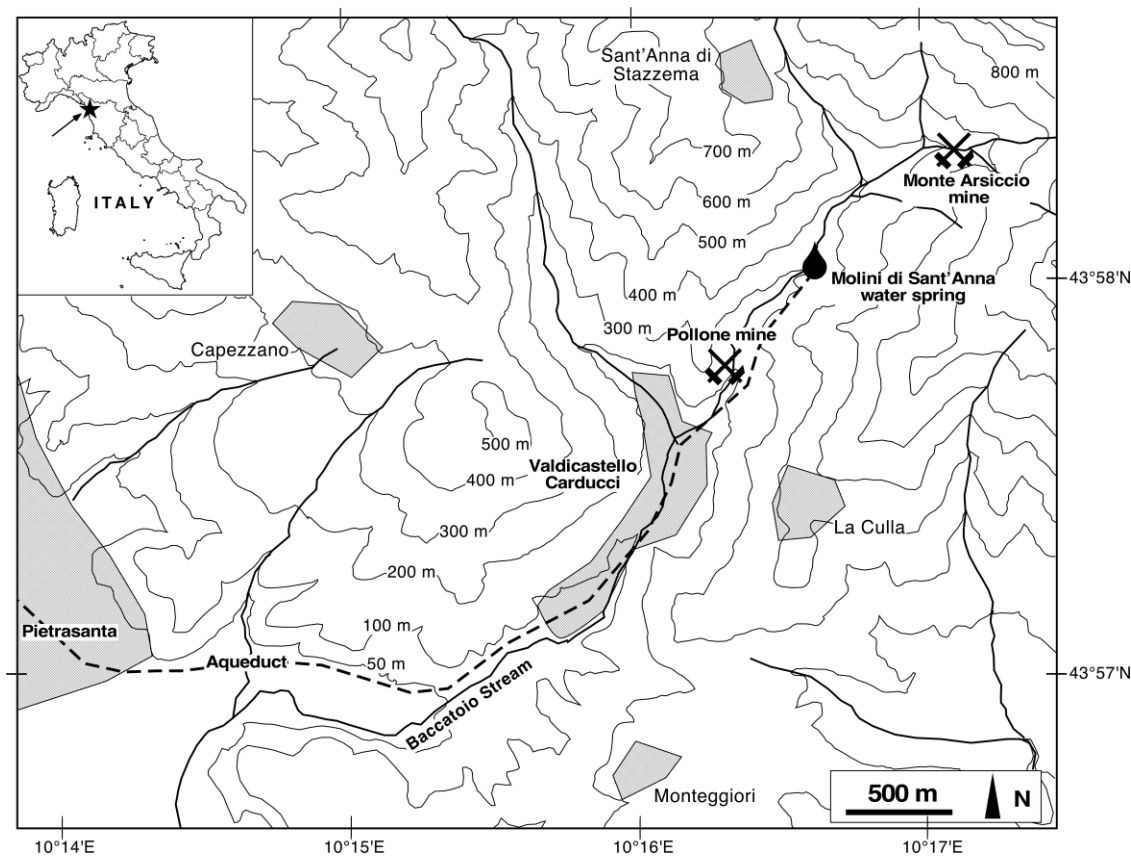
113 Valdicastello Carducci, in the southern sector of the Apuan Alps. The mining sites are distributed in

114 the catchment area of the Baccatoio stream and very close to the watercourse itself. The Baccatoio

115 stream (about 11 km in length) originates from the drainage of an abandoned tunnel of one of the

116 main mines, receives additional drainages, crosses Valdicastello Carducci and the Versilia Plain and

117 flows into the Ligurian Sea (Perotti et al., 2017).



118

119 **Figure 1.** Sketch map showing Valdicastello Carducci and the mining district.

120

121 *2.3. Samples collection*

122 Three water samples were collected during a sunny day from an acid drainage located in the upper
123 part of the Monte Arsiccio mine (named “AMD”), from the Baccatoio immediately downstream the
124 confluence with the drainage (named “stream water”), and from the contaminated water spring
125 “Molini di Sant’Anna”. Samples were collected in duplicate in HDPE bottles (Nalgene®, Nalge
126 Nunc International, Rochester, USA) filled to the top (50 mL). For each sample, to one aliquot
127 DTPA (5 mmol/L) with HNO₃ (0.2 mol/L) was added in situ.

128 In order to gain insights on the formation of Tl(III) in AMD water samples, a synthetic solution of
129 TlNO₃ and FeNH₄(SO₄)₂ in 10 mmol/L H₂SO₄ (pH = 2.1) was prepared, intended as a simplified
130 model with respect the natural mine waters.

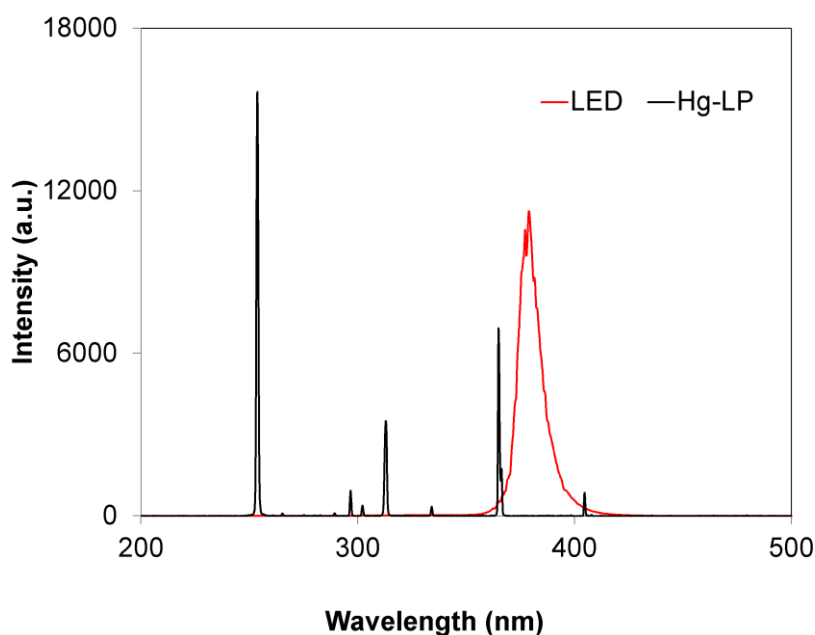
131 Two segments of the aqueduct pipeline serving the village of Valdicastello Carducci were taken
132 immediately before (inlet) and immediately after (outlet) a water chlorination treatment plant.
133 About 10 g of rust scales were taken from each pipeline sample and finely powdered in agate
134 mortar and pestle.

135

136 *2.4 Light sources*

137 Irradiation with sunlight was obtained by exposing the system for 8 h on a sunny day (average solar
138 irradiance 224 W/m², maximum solar irradiance 749 W/m²).

139 A low-pressure mercury UV bench lamp (254 nm, 8 W, Hg-LC170, PureLab classic mk2, ELGA,
140 UK), originally manufactured as an effective sterilization and sanitation instrument, was used for
141 UV irradiation. A low cost LED370E Ultra Bright Deep Violet (ThorLab, Germany) emitting at
142 379 nm was employed. Figure 2 shows the emitted lines of the two lamps measured by an
143 AvaSpec-2048-FT-SPU spectrometer (Avantes) set for a 170–439 nm spectral range in combination
144 with a 0.5 m optical fiber (Avantes, FC-UV400-0.5-SR). Samples were placed perpendicular to the
145 light source at a distance of 18.5 cm to the water surface.



146
 147 **Figure 2.** Emission spectra of the LED370E Ultra Bright Deep Violet LED (red) and the low pressure Hg
 148 lamp (black).

149

150 *2.5 Samples treatment*

151 *Aqueous samples.* Each water sample was collected in duplicate: one aliquot was stored without any
 152 chemical preservative for Tl(III), the second was spiked in situ with DTPA to investigate thallium
 153 speciation (Campanella et al., 2017). All aliquots were stored at 4°C.

154 Samples collected with DTPA were eventually filtered by 0.20 µm in laboratory and analyzed by
 155 IC-ICP-MS. Samples collected without any additive and the synthetic solution were distributed in
 156 10 mL HDPE bottles for irradiation experiments. Continuous magnetic stirring assured a good
 157 mixing of the sample solution. After 8 or 12 h of exposure, an aliquot of sample was collected,
 158 filtered at 0.20 µm and diluted in 5 mmol/L HNO₃ – 5 mmol/L DTPA within 5 minutes after the
 159 ending of irradiation before the analysis. The time between termination of the experiment until
 160 analysis or conservation of the sample was kept at a practical minimum, less than 5 minutes.

161 Diluted samples were kept at 4°C and analyzed within 24 h.

162 *Pipelines rust.* About 100 mg of powdered samples were dispersed in 5 mL of various solvents (see
 163 Table 1). The suspensions were sonicated for 1 min and left for 24 h at room temperature. In some

164 experiments the supernatant was filtered at 0.20 μm with RC membrane filters and stored in plastic
165 vials.

166

167 *2.6 IC-ICP-MS analysis*

168 An Agilent 7700x ICP-MS (Agilent Technologies, USA) with a MicroMist nebulizer and a Peltier
169 cooled (2°C) quartz Scott-type double pass spray chamber was used for the detection of ^{203}Tl and
170 ^{205}Tl . The operating parameters for ICP-MS were optimized prior to the determinations with a
171 tuning solution (Agilent Technologies, Tokyo, Japan) containing 1.0 ng/mL of Ce, Co, Li, Mg, Tl
172 and Y in 2% HNO_3 . A solution of 10 $\mu\text{g/L}$ of Ir in 2% HNO_3 was used as internal standard.

173 Redox Tl speciation was carried out by IC-ICP-MS using a cation exchange guard-column Dionex
174 CG-2 (4.0 mm i.d. 50 mm length). A high-pressure LC pump (1260 model, Agilent, USA) equipped
175 with a 1260 autosampler was used. The mobile phase was 5 mmol/L HNO_3 with 3 mmol/L
176 NH_4NO_3 and 0.75 mmol/L DTPA. The injection volume was 20 μL and the pump flow rate was set
177 at 1.5 mL/min. Limit of detection (LOD), defined as the minimum measured concentration
178 distinguishable from blank, as low as 0.05 $\mu\text{g}\cdot\text{L}^{-1}$ was achieved for Tl(I) and Tl(III)-DTPA.

179

180 *2.7 Iron(II) detection and physico-chemical parameters measurements*

181 The presence of Fe(II) in samples and standard solutions was spectrophotometrically detected by
182 complexation with TPTZ following the procedure of Krishnamurti and Huang (Krishnamurti and
183 Huang, 1990). Briefly, 1.4 mL of sample was added to 0.1 mL of hydrochloric acid (6 mol/L).
184 Then, 0.2 mL of NH_4F (2 mol/L), 0.2 mL of TPTZ (2.4 mmol/L in 0.12 mol/L HCl), and 0.4 mL of
185 ammonium acetate buffer (2 mol/L, pH 4.5), were added in this order. The presence of iron(II) is
186 indicated by the formation of the intense violet complex (λ_{max} 597 nm).

187

188

189 **3. Results**

190 *3.1 Characterization of AMD and water sample from Baccatoio stream*

191 The content of total thallium in the collected AMD and in stream water samples, determined by
192 ICP-MS, was 948 ± 42 $\mu\text{g/L}$ and 153 ± 5 $\mu\text{g/L}$, respectively.

193 In AMD sample spiked with DTPA only Tl(I) was detected, while in the stream water sample we
194 found by IC-ICP-MS analysis that Tl(III) was 39.9% of total Tl (61 ± 1 $\mu\text{g/L}$). This result is in
195 agreement with the results of our previous work (Campanella et al., 2017). The filtration of both
196 AMD and stream water samples through 0.20 μm membrane filter did not produce total Tl values
197 significantly different from the amount of total Tl found in unfiltered samples. This indicates that in
198 the two collected samples, Tl(III) exists in chemical forms soluble in the DTPA-HNO₃ system.

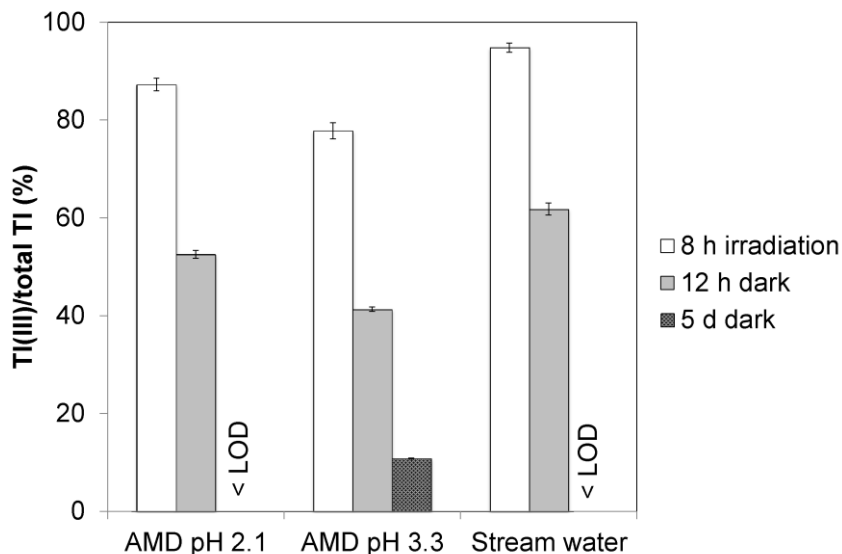
199 Without DTPA addition, the initial redox distribution of Tl(I)/Tl(III) was not preserved, and the
200 amount of Tl(I) detected by IC-ICP-MS was not significantly different from the total Tl quantified
201 by ICP-MS. The aliquots collected without DTPA were employed for the redox experiments
202 described in the following paragraphs.

203

204 *3.2 Effect of light sources on AMD and stream water samples and on aqueous model system*

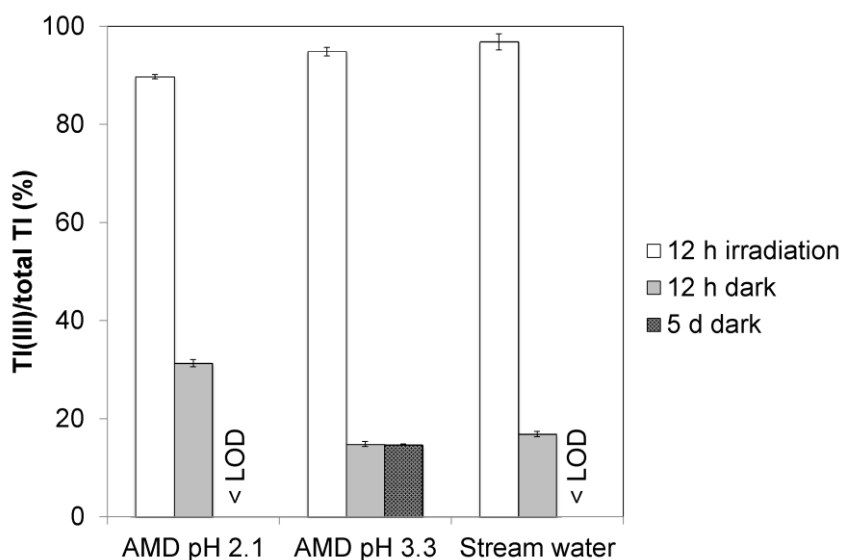
205 In samples exposed to sunlight, a consistent oxidation of Tl(I) to Tl(III) was observed (see white
206 bars in Figure 3); the mass balance was maintained during this time span with no significant
207 changes in total thallium concentration.

208 The effect of pH on Tl(I) oxidation was evaluated by increasing the pH of AMD from 2.1 to 3.3
209 with saturated sodium carbonate. After increasing the pH, the sample was exposed to sunlight and
210 also in this case almost 80 % Tl(III) with respect total thallium was detected (Figure 3).

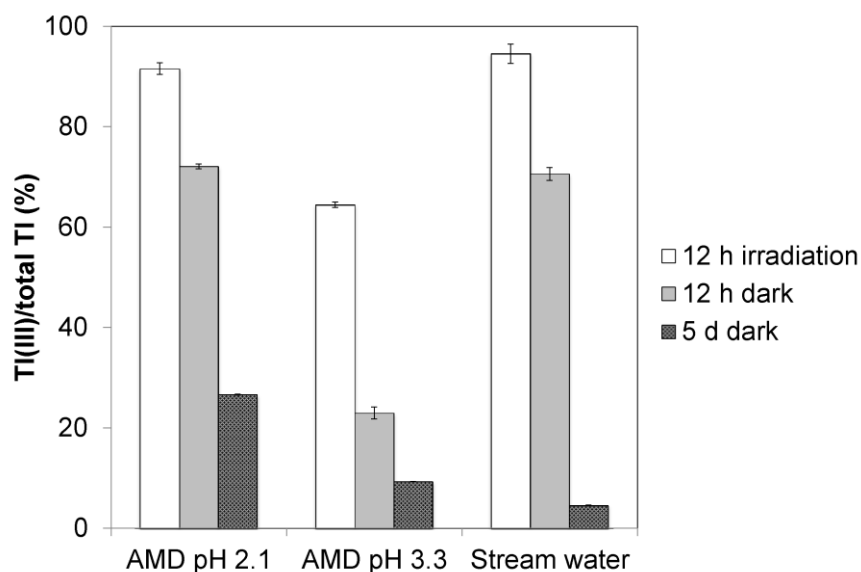


211
 212 **Figure 3.** Percentage of Tl(III) respect to total thallium found by IC-ICP-MS in not filtered samples
 213 exposed for 8 h to sunlight (white bars), followed by 12 h (grey bars) and 5 d (spotted bars) in the dark.
 214 Errors are reported as relative standard deviation calculated from 3 repeated measures.

215
 216 Samples were then exposed to other two sources of light: a low-pressure UV lamp and a light
 217 emitting diode. In both cases, after 12 h more than 80 % of total Tl was detected as Tl(III) (see
 218 white bars in Figure 4 and 5).



219
 220 **Figure 4.** Percentage of Tl(III) respect to total thallium found by IC-ICP-MS in real samples exposed for
 221 12 h to UV light (white bars), followed by 12 h (grey bars) and 5 d (spotted bars) in the dark. Errors are
 222 reported as relative standard deviation calculated from 3 repeated measures.



223
224

Figure 5. Percentage of Tl(III) respect to total thallium found by IC-ICP-MS in real samples exposed for

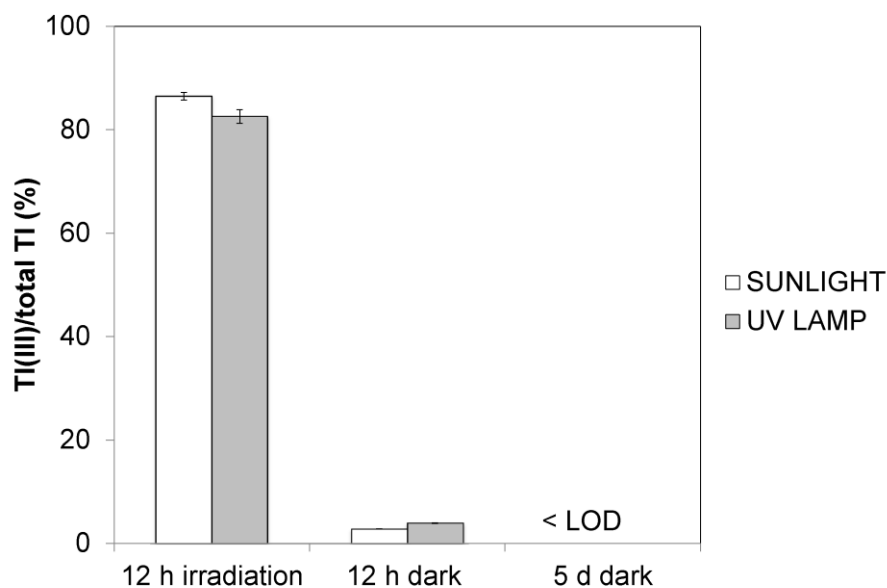
225 12 h to a light emitting diode (white bars), followed by 12 h (grey bars) and 5 d (spotted bars) in the dark.
226 Errors are reported as relative standard deviation calculated from 3 repeated measures.

227

228 The exposure to light sources was followed by 12 h (grey bars in Figures 3-5) and 5 d (dotted bars
229 in Figures 3-5) of storage in the dark. The removal of the light source caused, in all the cases, the
230 progressive back reduction of Tl(III) to Tl(I), even if with different kinetics. The highest reduction
231 rate was observed in samples exposed to the UV lamp, followed by samples exposed to sunlight and
232 then to LED. In all cases, a consistent fraction of Tl(III) (from 40 to 70 % of total Tl) was still
233 present in solution after 12 h. After 5 d Tl(III) was below the method detection limit (50 ng/g) in
234 samples previously exposed to sunlight and UV lamp, with the exception of the AMD sample at pH
235 3.3. In samples exposed to LED, still 4.5 – 29% Tl(III) (respect to total Tl) was present in solution.

236

237 In the synthetic solution, a comparable extent of Tl(I) → Tl(III) oxidation was obtained after the
238 exposure to sunlight or UV irradiation (Figure 6). However, the reduction of Tl(III) to Tl(I)
239 proceeded faster compared with natural samples (see Figure 3 and 4), and after 12 h in the dark less
240 than 3% Tl(III) persisted in solution.



241
 242 **Figure 6.** Percentage of Tl(III) respect to total thallium found by IC-ICP-MS in Tl(I)-Fe(III) standard
 243 solution exposed for 8 h to sunlight or for 12 h to UV light, followed by 12 h and 5 d in the dark (white bars:
 244 sunlight; grey bars: UV light). Errors are reported as relative standard deviation calculated from 3 repeated
 245 measures.

246

247 Unlike what we observed in natural samples, no oxidation of Tl(I) to Tl(III) occurred when the
 248 standard solution was exposed to 12 h LED irradiation. Thus, it is argued that in natural waters
 249 more chemical species, other than Fe(III)/Fe(II), are involved in Tl(I) oxidation. Under light
 250 illumination, electrons might be transferred from Tl(I) to Fe(III) through a ligand-to-metal charge-
 251 transfer process, which could be greatly influenced by the type of ligands coordinated to Fe(III). It
 252 is reported that over 99% of dissolved iron may be complexed to organic matter in natural waters,
 253 greatly increasing the solubility of iron and preventing the precipitation of oxyhydroxides (Su et al.,
 254 2015). Iron(III) organic complexes, such as Fe-oxalate, Fe-citrate and Fe-fulvic acid (the fraction
 255 of humic acids soluble at low pH) can be photolyzed to generate reactive species, such as $O_2^{\cdot-}$,
 256 H_2O_2 , $\cdot OH$ (Kong and He, 2016). Thus, we separately added to the Tl(I)+Fe(III) synthetic solution
 257 these three organic compounds: citric (1 mmol/L), oxalic (1 mmol/L) and fulvic acid (10 mg/L).
 258 Irradiation experiments with LED were repeated, revealing that only the addition of soil fulvic acid
 259 produced a signal of Tl(III) significantly different from the blank (5.6 $\mu g/L$, corresponding to the

260 0.9 % of total thallium). However, the signal intensity was not sufficient to justify the almost
261 quantitative oxidation observed in natural samples.

262 Besides organic acids, Fe(III) is able to form complexes with a wide range of inorganic compounds,
263 including arsenic(V) (Chai et al., 2017). Taking into account that waters from AMD contain up to 1
264 mg/L of arsenic, the effect of Fe(III)+As(V) on Tl(I) oxidation was evaluated. The addition of 1
265 mg/L As(V) (prepared with high purity As₂O₅ and water) produced, under LED irradiation, the
266 oxidation of 70% Tl(I). After 12 h in the dark, 10.8% Tl(III) was still detected.

267 Therefore, the system composed by Fe(III)+As(V)+Tl(I) at pH = 2.1 (H₂SO₄) is the model that can
268 reproduce more closely the results of natural samples.

269 The original iron concentrations in natural samples were measured with ICP-MS (1937 mg/L and
270 318 mg/L in AMD and stream sample, respectively; relative standard deviation < 5%).

271 Before and after irradiation with each light source, the presence of Fe(II) was evaluated both in
272 samples and in the synthetic solution, by exploiting the selective formation of a coloured complex
273 between Fe(II) and TPTZ. In both real samples, a small initial concentration of Fe(II) was detected,
274 equal to 0.08 and 0.18 mg/L for stream water and AMD, respectively. Successively to the
275 irradiation with solar light, UV and LED, in both samples a concentration higher than 5 mg/L, and
276 thus not correlated with total thallium concentration, was detected. Iron(II) was present also in the
277 Tl(I)+Fe(III) standard solution exposed to sunlight and UV source while it was not detected in the
278 LED experiment. In addition, the presence of Fe (II) in the Fe(III)+As(V)+Tl(I) standard after LED
279 irradiation was clearly detected .

280

281 *3.3 Tl redox state and reactivity in pipelines*

282 A source of Tl contamination, directly related to the human exposure (Campanella et al., 2016), was
283 found in the crust deposited in the pipeline of the aqueduct system of the Valdicastello Carducci
284 village. Crust samples were scraped from two pipeline segments removed from the drinking water
285 distribution system, respectively before and after a disinfection system.

286 Total thallium analysis by microwave digestion with nitric acid/H₂O₂ and ICP-MS gave 0.31 and
287 42.5 mg/g of thallium in the pre- and post-water treatment pipeline, respectively. The recovery of
288 total thallium after leaching with 5 mmol/L DTPA + 2 wt% HNO₃ was 98.2% (0.30 mg/g) and
289 92.7% (39.4 mg/g), respectively.

290 Table 1 shows the results of the different leaching experiments on pipeline crusts. The leaching
291 tests were conducted by suspending 100 mg of rust into 5 mL of different solutions for 24 h at room
292 temperature in the dark. In addition to the percentage of extracted thallium in the leached solution,
293 for each experiments the thallium speciation is also reported.

294 The results of leaching by deionized(milliQ) indicate that 6.6% (0.021 mg/g) and 12.1% (4.7 mg/g)
295 of the total thallium contained in the pre- and post-water treatment pipeline is soluble in water at
296 neutral pH. The leaching with tap water slightly increased the amount of thallium in solution (0.028
297 mg/g and 5.04 mg/g in the pre- and post-water treatment pipeline).

298 Three oxidants commonly used in water treatment systems, i.e. sodium hypochlorite and hydrogen
299 peroxide with or without acetic acid, were tested to evaluate their effect on thallium speciation in
300 rust scale. The amount of thallium in solution with respect to leaching in water decreased after
301 treatment with 0.16 mol/L NaClO down to 4.3% (0.013 mg/g) and 6.3% (2.6 mg/g) with respect
302 total thallium measured after microwave digestion. In addition Tl(III) was not detected in solution.
303 On the other hand, treatment with 1.5 wt% H₂O₂ or 1.5 wt% H₂O₂ + 0.5 wt% acetic acid (acetic
304 acid was added to mimic the use of peracetic acid, another common disinfectant), with respect to
305 leaching in water, increased the percentage of total thallium in solution up to 21.7% (0.067 mg/g)
306 and 72% (28.5 mg/g) in the pre- and post-water treatment pipeline, respectively. However these
307 treatments did not influence the thallium speciation.

308

309

310

311 **Table 1.** Results from leaching experiments on 100 mg pipeline rust in 5 mL solution (pre = pipeline
 312 removed before the water treatment plant; post = pipeline removed after the water treatment plant).

| Leaching experiment | Tl(III) mg/L (IC-ICP-MS) | Tl(I) mg/L (IC-ICP-MS) | Total Tl mg/L (ICP-MS) | % extraction ^a |
|--|-----------------------------|---------------------------|---------------------------|---------------------------|
| <i>Pre + deionized water</i> | ND ^b | 0.41 | 0.43 | 6.6 |
| <i>Pre + tap water</i> | ND | 0.55 | 0.52 | 8.9 |
| <i>Pre + DTPA/HNO₃</i> | 0.1 | 6.0 | 6.1 | 97 |
| <i>Pre + NaClO</i> | ND | 0.26 | 0.28 | 4.1 |
| <i>Pre + H₂O₂</i> | ND | 1.07 | 1.1 | 17 |
| <i>Pre + H₂O₂/acetic acid</i> | ND | 1.62 | 1.5 | 26 |
| <i>Post + deionized water</i> | ND | 95 | 95 | 11 |
| <i>Post + tap water</i> | ND | 101 | 102 | 12 |
| <i>Post + DTPA/HNO₃</i> | 48 | 740 | 788 | 93 |
| <i>Post + NaClO</i> | ND | 51 | 50 | 6.1 |
| <i>Post + H₂O₂</i> | ND | 571 | 570 | 67 |
| <i>Post + H₂O₂/acetic acid</i> | 1.1 | 569 | 571 | 67 |

313 ^aPercentage of extraction with respect to total thallium determined after acid-microwave digestion (6.24 mg/L and
 314 849.28 mg/L in pre- and post-water treatment plant, respectively).

315 ^bNot detected (below detection limit, i.e. 0.05 µg/L).

316

317 Speciation analysis, in samples treated with DTPA+HNO₃, revealed that in the pre-implant pipeline
 318 a low amount of Tl(III) (0.5 ng/g) was present, while in the post-implant pipeline Tl(III) was 2.4
 319 mg/g (6% of total thallium).

320 The treatment with 0.16 mol/L NaClO was replicated on a sample collected from the thallium-
 321 contaminated water spring that until 2014 has been used to feed the public aqueduct of
 322 Valdicastello. The concentration of total thallium in this sample was 11.5 µg/L (±0.3 µg/L), and
 323 from IC-ICP-MS analysis it resulted composed only by Tl(I). The treatment with H₂O₂ or
 324 H₂O₂/acetic acid did not influence thallium speciation. After the addition of NaClO, the analysis of

325 the sample filtered (through 0.22 μm membrane filter) and treated with DTPA+HNO₃ showed
326 thallium levels below the detection limit of the method. The analysis of the same sample, firstly
327 treated with DTPA+HNO₃ and successively filtered, revealed the presence of Tl(III) with a
328 conversion yield of 94.8% with respect to original Tl(I).

329

330

331 **4. Discussion**

332 As far as the redox chemistry of thallium is concerning, Tl(I) is the dominant species expected in
333 waters in past-mining settings (Casiot et al., 2011), even if the dynamics of Tl(I) –Tl(III) redox
334 reactions in these environments remains to be fully elucidated. Indeed, as reported in a previous
335 work (Campanella et al., 2017), speciation analysis revealed the occurrence of Tl(III) in water
336 samples from Baccatoio stream, even if the acid drainages spilling in the stream contain Tl(I) as the
337 only detectable species.

338 It has to be noted that other authors detected Tl(III) in notable amount in natural waters. In 1975,
339 Batley and Florence (1975) found that up to 80% of soluble thallium in seawater was present as
340 anionic Tl(III) complexes. Later, Lin and Nriagu (Lin and Nriagu, 1999) found that in the Great
341 Lakes of the United States Tl(III) ranges from 43% to 73% of the total dissolved thallium.

342 The first set of experiments, presented in section 3, was aimed to rationalize the thallium oxidation
343 process taking place in the Baccatoio stream catchment. In our experiments we observed that the
344 tested light sources oxidised almost quantitatively Tl(I) to Tl(III) within 12 h in the AMD and
345 stream water sample. Thallium(III) was fairly stable within 12 h after the removal of the light
346 source, and after 5 d in the dark it was still detected in samples previously exposed to LED and UV
347 sources.

348 Oldenburg and co-workers (1997) and Horváth and co-workers (1999) studied the photochemical
349 reaction mechanism of thallium in strongly alkaline solution by irradiating TlClO₄ in 1 mol/L

350 NaOH solution using a high pressure UV light. The irradiated solution yielded a yellow-brown
351 suspension, and the same result was obtained by Li and co-workers in neutral solutions (2005).
352 Karlsson and co-workers. (2006) also verified that UV light produced Tl(III) in standard solutions
353 of Tl(I) and Fe(III).

354 Inspired by these findings and in order to confirm the role of photooxidation in the Baccatoio-AMD
355 system, oxidation was tested in a Tl(I) synthetic solution in the presence of Fe(III) and sunlight or
356 UV light. Contrary to natural samples, in the synthetic solution Tl(III) that formed in the synthetic
357 solution was reduced back to Tl(I) after the removal of the light source rather quickly. Furthermore,
358 an unexpected result was the resistance to oxidation of Tl(I) exposed to visible light emitted by the
359 deep violet LED, differently to what was observed in natural waters. The addition of As(V) together
360 with Fe(III) in the synthetic solution promoted the formation of Tl(III), with a reaction mechanism
361 that might involve aqueous Fe(III)-As(V) complexes (Chai et al., 2017).

362 The detection of Fe(II) even in a synthetic solution composed only of Fe(III) in 5 mmol/L H₂SO₄,
363 after irradiation with UV and solar light indicated that there is not a direct electron transfer between
364 iron and thallium. It is known, indeed, that in aqueous solutions Fe(III) alone undergoes cyclic
365 photochemical reduction to Fe(II) when irradiated with UV light (Feng and Nansheng, 2000).

366 On the basis of these experiments we can state that the distribution of Tl(I) and Tl(III) in natural
367 waters likely depend highly on the presence of aqueous cations (e.g., Fe(III) or As(V)), pH and UV
368 light.

369 A connection between environmental threats and waterborne human diseases has been since long
370 recognized (e.g. McMichael, 1994). In the case of the past-mining impacted Baccatoio basin,
371 Biagioni and co-workers (2017) recently found solid Tl(III) and Tl(I)-phases represented by Tl₂O₃
372 and TlCl in rust scales from pipelines of the Valdicastello Carducci waterwork, since long fed by
373 Tl(I)-contaminated waters. They attributed the Tl(I) oxidation and Tl₂O₃ particle precipitation to
374 water chlorination in a treatment plant. Our results confirm this hypothesis.

375 A series of leaching experiments were performed on rust scales removed from pipeline segments
376 taken before and after the Valdicastello Carducci public water-treatment plant, with the aim to
377 evaluate i) how much thallium contained in the scales may dissolve into water, ii) which is the form
378 of soluble thallium and iii) thallium reactivity. The results indicated that a minor but significant
379 fraction of thallium is released from scales to both deionized and tap waters, in the sole form of
380 Tl(I), and that the amount is higher in the pipeline after the treatment plant. This thallium likely
381 originated from Tl(I) chloride dissolution ($K_{sp} = 10^{-3.65}$) (Xiong, 2009), in agreement with the
382 observation that Tl(III) oxide is rather insoluble in water ($K_{sp} = 10^{-5.8}$ mol/L at pH 7 and $10^{-11.7}$
383 mol/L at pH 9) (Nagy et al., 2005; Xiong, 2009). From the data of Schindler (1958) the solubility
384 product of Tl_2O_3 for the reaction $Tl_2O_3 + 6H^+ \rightarrow 2Tl^{3+} + 3H_2O$ in 3.5 mol/L $NaClO_4$ is $K_{sp} =$
385 $10^{-2.34}$, and the solubility equilibrium may be further altered if complexing agents are present in
386 solution.

387 Leaching with DTPA and nitric acid revealed that both Tl(I) and Tl(III) can be extracted from
388 scales, in particular in the pipeline downstream the treatment plant. Since scales may act as a
389 secondary source for thallium release in drinkable waters, it is important to investigate possible
390 remediation actions (McMichael, 1994). Redox methods may contribute to immobilize thallium in
391 the form of Tl(III) in scales, reducing its mobility to waters. Different oxidants, suitable for
392 drinking water treatments, were tested, and the best results were obtained by using sodium
393 hypochlorite. In an alternative way, if planned actions focus on thallium removal from scales, our
394 results indicate that both Tl(I) and Tl(III) may be efficiently extracted from rusts by using
395 EDTA+HNO₃ as washing solution.

396

397

398 **5. Conclusion**

399 To date, literature cannot explain the behaviour of thallium and its speciation in the aqueous media
400 and in even more complex natural systems. The difficulties in reconciling thermodynamic

401 predictions and speciation analytical data are confirmed in our previous work, where we reported
402 the finding of Tl(III) in natural waters (Campanella et al., 2017). This paper can be considered as a
403 step forward in the comprehension of Tl(I) and Tl(III) behaviour in real contaminated systems. In
404 summary, we demonstrated that the concentration and thus the distribution of Tl(I) and Tl(III) is
405 affected by radiation and aqueous Fe(III). In absence of Fe(III), no oxidation takes place. In the
406 acid conditions (pH around 2) of both AMD and surface water samples, Tl(III) remained in solution
407 or formed nanoparticulate with dimension less than 200 nm. The oxidation process was reversible,
408 and the reduction showed a slower kinetics in real samples respect to model standard solutions.
409 When a solution of Tl(I) was irradiated with a LED source, which emits at the boundaries of the UV
410 spectrum (378 nm), Fe(III) was not sufficient to promote the oxidation and the presence of other
411 elements (e.g. arsenic(V) was investigated in this work) is necessary.

412 The treatment of water with 0.16 mol/L NaClO, which is a reasonable concentration for
413 potable/drinking water treatment, caused Tl(I) oxidation and precipitation in neutral environment as
414 Tl₂O₃ which remained fixed in pipeline encrustations. Thallium oxide is slowly released from the
415 pipelines representing an additional source of contamination.

416 This study puts in evidence the complexity of thallium geochemistry. The reduction and oxidation
417 reactions occurring in the studied AMD-stream system are critical for environmental and health
418 reasons, both for the different toxicity attributed to the monovalent and trivalent forms and in view
419 of a mandatory environmental remediation. Furthermore, the results of this work could be useful for
420 the rational development and design of specific water treatment plants, aimed to avoid a “chronic”,
421 constant thallium contamination in water pipelines.

422 **References**

- 423 Allen, J.M., Lucas, S., Allen, S.K., 1996. Formation of hydroxyl radical (\cdot OH) in illuminated
424 surface waters contaminated with acidic mine drainage. *Environ. Toxicol. Chem.* 15, 107–113.
- 425 Batley, G.E., Florence, T.M., 1975. Determination of thallium in natural waters by anodic stripping
426 voltammetry. *J. Electroanal. Chem. Interfacial Electrochem.* 61, 205–211.
- 427 Belzile, N., Chen, Y.-W., 2017. Thallium in the environment: A critical review focused on natural
428 waters, soils, sediments and airborne particles. *Appl. Geochemistry* 84, 218–243.
- 429 Biagioni, C., D’Orazio, M., Lepore, G.O., d’Acapito, F., Vezzoni, S., 2017. Thallium-rich rust
430 scales in drinkable water distribution systems: A case study from northern Tuscany, Italy. *Sci.*
431 *Total Environ.* 587, 491–501.
- 432 Campanella, B., Casiot, C., Onor, M., Perotti, M., Petrini, R., Bramanti, E., 2017. Thallium release
433 from acid mine drainages: Speciation in river and tap water from Valdicastello mining district
434 (northwest Tuscany). *Talanta* 171. doi:10.1016/j.talanta.2017.05.009
- 435 Campanella, B., Onor, M., D’Ulivo, A., Giannecchini, R., D’Orazio, M., Petrini, R., Bramanti, E.,
436 2016. Human exposure to thallium through tap water: A study from Valdicastello Carducci
437 and Pietrasanta (northern Tuscany, Italy). *Sci. Total Environ.* 548–549.
438 doi:10.1016/j.scitotenv.2016.01.010
- 439 Chai, L., Yang, J., Zhang, N., Wu, P.-J., Li, Q., Wang, Q., Liu, H., Yi, H., 2017. Structure and
440 spectroscopic study of aqueous Fe (III)-As (V) complexes using UV–Vis, XAS and DFT-
441 TDDFT. *Chemosphere* 182, 595–604.
- 442 Cvjetko, P., Cvjetko, I., Pavlica, M., 2010. Thallium toxicity in humans. *Arh. Hig. Rada Toksikol.*
443 61, 111–118.
- 444 D’Orazio, M., Biagioni, C., Dini, A., Vezzoni, S., 2017. Thallium-rich pyrite ores from the Apuan
445 Alps, Tuscany, Italy: constraints for their origin and environmental concerns. *Miner. Depos.*
446 52, 687–707.
- 447 Davies, M., Figueroa, L., Wildeman, T., Bucknam, C., 2016. The oxidative precipitation of thallium

448 at alkaline pH for treatment of mining influenced water. *Mine Water Environ.* 35, 77–85.

449 Feng, W., Nansheng, D., 2000. Photochemistry of hydrolytic iron (III) species and photoinduced
450 degradation of organic compounds. A minireview. *Chemosphere* 41, 1137–1147.
451 doi:10.1016/S0045-6535(00)00024-2

452 Gadde, R.R., Laitinen, H.A., 1974. Heavy metal adsorption by hydrous iron and manganese oxides.
453 *Anal. Chem.* 46, 2022–2026.

454 Horváth, O., Stevenson, K.L., Vogler, A., 1999. Photoinduced electron ejection from hydroxo
455 complexes of thallium (I) and tin (II) in alkaline aqueous solution. *Radiat. Phys. Chem.* 55,
456 497–501.

457 Huangfu, X., Jiang, J., Lu, X., Wang, Y., Liu, Y., Pang, S.-Y., Cheng, H., Zhang, X., Ma, J., 2015.
458 Adsorption and oxidation of Thallium (I) by a nanosized manganese dioxide. *Water, Air, Soil*
459 *Pollut.* 226, 2272.

460 Kaplan, D., Mattigod, S., 1998. Aqueous geochemistry of thallium, in: Nriagu, J. (Ed.), *Thallium in*
461 *the Environment*. John Wiley & Sons Inc., New York, pp. 15–29.

462 Karlsson, U., Karlsson, S., Düker, A., 2006. The effect of light and iron (II)/iron (III) on the
463 distribution of Tl (I)/Tl (III) in fresh water systems. *J. Environ. Monit.* 8, 634–640.

464 Kong, L., He, M., 2016. Mechanisms of Sb (III) Photooxidation by the Excitation of Organic Fe
465 (III) Complexes. *Environ. Sci. Technol.* 50, 6974–6982.

466 Krishnamurti, G.S.R., Huang, P.M., 1990. Spectrophotometric determination of Fe(II) with 2,4,6-
467 tri(2'-pyridyl)-1,3,5-triazine in the presence of large quantities of Fe(III) and complexing ions.
468 *Talanta* 37, 745–748. doi:10.1016/0039-9140(90)80105-O

469 Lan, C.-H., Lin, T.-S., 2005. Acute toxicity of trivalent thallium compounds to *Daphnia magna*.
470 *Ecotoxicol. Environ. Saf.* 61, 432–435.

471 Li, D., Gao, Z., Zhu, Y., Yu, Y., Wang, H., 2005. Photochemical reaction of Tl in aqueous solution
472 and its environmental significance. *Geochem. J.* 39, 113–119.

473 Lin, T.-S., Nriagu, J.O., 1999. Thallium speciation in river waters with Chelex-100 resin. *Anal.*

474 Chim. Acta 395, 301–307.

475 McMichael, A.J., 1994. Global environmental change and human health: new challenges to scientist
476 and policy-maker. *J. Public Health Policy* 407–419.

477 Molina, L.C.P., Fréchou, D.M.S., Verstraeten, S. V, 2017. Early response of glutathione-and
478 thioredoxin-dependent antioxidant defense systems to Tl (I)-and Tl (III)-mediated oxidative
479 stress in adherent pheochromocytoma (PC12adh) cells. *Arch. Toxicol.* 1–17.

480 Nagy, P., Fischer, A., Glaser, J., Ilyukhin, A., Maliarik, M., Tóth, I., 2005. Solubility, complex
481 formation, and redox reactions in the Tl 2O₃-HCN/CN--H₂O system. Crystal structures of the
482 cyano compounds Tl(CN)₃·H₂O, Na[Tl(CN)₄]·3H₂O, K[Tl(CN)₄], and TlTlIII(CN)₄ and of
483 TlI₂C₂O. *Inorg. Chem.* 44, 2347–2357. doi:10.1021/ic0485918

484 Oldenburg, K., Vogler, A., Horváth, O., 1997. Diversity in photoredox chemistry of oxo or hydroxo
485 complexes of s₂ metal ions. *Inorganica Chim. Acta* 257, 149–151.

486 Osorio-Rico, L., Santamaria, A., Galván-Arzate, S., 2017. Thallium Toxicity: General Issues,
487 Neurological Symptoms, and Neurotoxic Mechanisms, in: *Neurotoxicity of Metals*. Springer,
488 pp. 345–353.

489 Paul, R.B., 2001. photochemical reactions and organic matter binding of mercuric ion and
490 methylmercury in surface water. *WRC Res.*

491 Peacock, C.L., Moon, E.M., 2012. Oxidative scavenging of thallium by birnessite: explanation for
492 thallium enrichment and stable isotope fractionation in marine ferromanganese precipitates.
493 *Geochim. Cosmochim. Acta* 84, 297–313.

494 Perotti, M., Petrini, R., D’Orazio, M., Ghezzi, L., Giannecchini, R., Vezzoni, S., 2017. Thallium
495 and Other Potentially Toxic Elements in the Baccatoio Stream Catchment (Northern Tuscany,
496 Italy) Receiving Drainages from Abandoned Mines. *Mine Water Environ.* 1–11.

497 Ralph, L., Twiss, M.R., 2002. Comparative toxicity of thallium (I), thallium (III), and cadmium (II)
498 to the unicellular alga *Chlorella* isolated from Lake Erie. *Bull. Environ. Contam. Toxicol.* 68,
499 261–268.

500 Rickwood, C.J., King, M., Huntsman-Mapila, P., 2015. Assessing the fate and toxicity of thallium I
501 and thallium III to three aquatic organisms. *Ecotoxicol. Environ. Saf.* 115, 300–308.
502 doi:10.1016/j.ecoenv.2014.12.024

503 Schindler, P., 1958. Löslichkeitsprodukte von Metalloxyden und- Hydroxyden. 2. Mitteilung. Das
504 Löslichkeitsprodukt des Thallium (III)- oxydes. *Helv. Chim. Acta* 41, 527–535.

505 Su, H., Yang, R., Zhang, A., Li, Y., 2015. Dissolved iron distribution and organic complexation in
506 the coastal waters of the East China Sea. *Mar. Chem.* 173, 208–221.

507 Xiong, Y., 2009. The aqueous geochemistry of thallium: speciation and solubility of thallium in low
508 temperature systems. *Environ. Chem.* 6, 441–451.

509 Zafiriou, O.C., Jousset-Dubien, J., Zepp, R.G., Zika, R.G., 1984. Photochemistry of natural waters.
510 *Environ. Sci. Technol.* 18, 358A–371A.

511