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

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ABSTRACT

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

In this work, water samples collected from the mine drainages and the contaminated stream were adopted as model to study the distribution of aqueous Tl(I)/Tl(III) as a function of light exposure and solution properties and composition. The influence of three light sources and organic acids was
evaluated. Thallium speciation was also assessed in tap water after treatment with common oxidizing agents, and in the rust crust collected from the public waterworks.

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

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

Thallium has two principal oxidation states, Tl(I) and Tl(III), both of which are considered highly toxic to living organisms: Tl(I) salts are very soluble and Tl\(^+\) is similar to potassium, so it is able to replace the latter during enzymatic reactions. Tl\(^{3+}\) induces an oxidative stress status in human cells and it was found to be considerably more toxic than Tl\(^+\) to the unicellular alga *Chlorella* (Molina et al., 2017; Osorio-Rico et al., 2017; Rickwood et al., 2015). Thallium(I) is expected to be the dominant species in aqueous solutions in equilibrium with atmospheric oxygen and in the absence of complexing agents (Lin and Nriagu, 1999). From a thermodynamic point of view, conversion of Tl(I) to Tl(III) would be expected only in the presence of extremely strong oxidants, such as MnO\(_4^-\) or Cl\(_2\), and high alkalinity (Kaplan and Mattigod, 1998).
A severe thallium contamination has been recently discovered in the acid mine drainages (AMDs) outflowing from tunnels in a past-mining area in the southern sector of the Apuan Alps (northern Tuscany, Italy) (Campanella et al., 2016). In the abandoned mining sites, bacteria-mediated oxidation of thallium-rich pyrite ores caused the production of iron(III) and hydrogen ions that catalytically dissolved pyrite, thereby increasing the metal load in the AMDs. The Baccatoio stream receives AMDs and crosses the Valdicastello Carducci village and the Versilia Plain, a densely populated area. Thallium contamination also affects waters from a spring outflowing in the Baccatoio catchment and until recently used for drinking water supply, so that this element became widespread into pipeline encrustations (Campanella et al., 2016; D’Orazio et al., 2017; Perotti et al., 2017). The content of thallium ranged from 0.05 to 1 µg/L in potable water from public fountain, from 0.7 to 48 µg/L in tap water from private houses, from 10 to 130 µg/L in the water of Baccatoio, and from 300 to 800 µg/L in AMDs (Campanella et al., 2017, 2016).

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

Metals oxidation cycles in natural waters are often mediated by photochemical processes (Allen et al., 1996; Zafiriou et al., 1984). Some authors observed that the oxidation of Tl(I) in aqueous solutions can take place during UV or sunlight irradiation (Karlsson et al., 2006; Li et al., 2005), thanks to the production of possible oxidative species such as hydrogen peroxide or ·OH (Paul, 2001). Especially the highly reactive transient hydroxyl radicals might represent strong oxidants, considering that the production of hydroxyl radicals is speeded up by Fe(II) generated by
photoreduction (photo-Fenton reactions). Indeed, AMDs in the Baccatoio mining area are characterized by high iron and manganese content, whose hydro-geochemistry is well known to be able to influence the oxidation state of thallium (Davies et al., 2016; Gadde and Laitinen, 1974; Huangfu et al., 2015; Peacock and Moon, 2012). The ability of Mn(IV) to oxidize Tl(I) is known (Huangfu et al., 2015), while no spontaneous oxidation of Tl(I) from Fe(III) is expected on thermodynamic grounds. In the case of iron, therefore, the combination with more chemical agents and radiation might be fundamental to explain oxidation reactions otherwise not spontaneous in natural systems.

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

2. Materials and methods

2.1 Reagents

High purity water (18.2 MΩ·cm) was obtained with an Elga Purelab-UV system (Veolia Environment, Paris, France). TraceCERT® nitric acid (HNO₃, 69%), sulphuric acid (H₂SO₄, ACS reagent 95-98%) iridium (analytical standard, 1000 mg/L Ir in 10 wt. % HCl), ammonium nitrate (NH₄NO₃ 99.999% trace metals basis), diethylenetriaminepentaacetic acid (DTPA), hydrogen peroxide (H₂O₂, 30%), acetic acid, sodium hypochlorite (NaClO, available chlorine 10-15%), ammonium fluoride (NH₄F), and manganese(IV) oxide (MnO₂ 50 wt.% on activated carbon) were purchased from Sigma-Aldrich. Arsenic(V) standard solution and ammonium iron(III) sulphate salt were purchased from Carlo Erba (Italy). Standard solutions of Tl(I) were prepared by dilution of 1000 mg/L Tl in 0.5 mmol/L HNO₃ (Merck) in the eluent phase. Standard solution of Tl(III) was prepared dissolving Tl(NO₃)₃·3H₂O (Sigma-Aldrich) in 5 mmol/L HNO₃ – 5 mmol/L DTPA. For
colorimetry of iron(II), 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ, ≥98%) obtained from Sigma-Aldrich was used as the complexing reagent. PTFE filters (4 mm thickness and 0.20 μm pore diameter, Sigma Aldrich) were chosen for the filtration.

2.2. Valdicastello Carducci and mining district

Figure 1 shows the area object of the study, located in the northwest of Tuscany (Italy). Valdicastello Carducci is a small village having about 1000 inhabitants. From the end of the World War II to 1990 an intense mining activity characterized the mountainous area immediately north of Valdicastello Carducci, in the southern sector of the Apuan Alps. The mining sites are distributed in the catchment area of the Baccatoio stream and very close to the watercourse itself. The Baccatoio stream (about 11 km in length) originates from the drainage of an abandoned tunnel of one of the main mines, receives additional drainages, crosses Valdicastello Carducci and the Versilia Plain and flows into the Ligurian Sea (Perotti et al., 2017).

Figure 1. Sketch map showing Valdicastello Carducci and the mining district.
2.3. Samples collection

Three water samples were collected during a sunny day from an acid drainage located in the upper part of the Monte Arsiccio mine (named “AMD”), from the Baccatoio immediately downstream the confluence with the drainage (named “stream water”), and from the contaminated water spring “Molini di Sant’Anna”. Samples were collected in duplicate in HDPE bottles (Nalgene®, Nalge Nunc International, Rochester, USA) filled to the top (50 mL). For each sample, to one aliquot DTPA (5 mmol/L) with HNO$_3$ (0.2 mol/L) was added in situ.

In order to gain insights on the formation of Tl(III) in AMD water samples, a synthetic solution of TlNO$_3$ and FeNH$_4$(SO$_4$)$_2$ in 10 mmol/L H$_2$SO$_4$ (pH = 2.1) was prepared, intended as a simplified model with respect the natural mine waters.

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

2.4 Light sources

Irradiation with sunlight was obtained by exposing the system for 8 h on a sunny day (average solar irradiance 224 W/m$^2$, maximum solar irradiance 749 W/m$^2$).

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

2.5 Samples treatment

Aqueous samples. Each water sample was collected in duplicate: one aliquot was stored without any chemical preservative for Tl(III), the second was spiked in situ with DTPA to investigate thallium speciation (Campanella et al., 2017). All aliquots were stored at 4°C. Samples collected with DTPA were eventually filtered by 0.20 µm in laboratory and analyzed by IC-ICP-MS. Samples collected without any additive and the synthetic solution were distributed in 10 mL HDPE bottles for irradiation experiments. Continuous magnetic stirring assured a good mixing of the sample solution. After 8 or 12 h of exposure, an aliquot of sample was collected, filtered at 0.20 µm and diluted in 5 mmol/L HNO₃ – 5 mmol/L DTPA within 5 minutes after the ending of irradiation before the analysis. The time between termination of the experiment until analysis or conservation of the sample was kept at a practical minimum, less than 5 minutes. Diluted samples were kept at 4°C and analyzed within 24 h.

Pipelines rust. About 100 mg of powdered samples were dispersed in 5 mL of various solvents (see Table 1). The suspensions were sonicated for 1 min and left for 24 h at room temperature. In some
experiments the supernatant was filtered at 0.20 μm with RC membrane filters and stored in plastic vials.

2.6 IC-ICP-MS analysis

An Agilent 7700x ICP-MS (Agilent Technologies, USA) with a MicroMist nebulizer and a Peltier cooled (2°C) quartz Scott-type double pass spray chamber was used for the detection of $^{203}$Tl and $^{205}$Tl. The operating parameters for ICP-MS were optimized prior to the determinations with a tuning solution (Agilent Technologies, Tokyo, Japan) containing 1.0 ng/mL of Ce, Co, Li, Mg, Tl and Y in 2% HNO$_3$. A solution of 10 µg/L of Ir in 2% HNO$_3$ was used as internal standard.

Redox Tl speciation was carried out by IC-ICP-MS using a cation exchange guard-column Dionex CG-2 (4.0 mm i.d. 50 mm length). A high-pressure LC pump (1260 model, Agilent, USA) equipped with a 1260 autosampler was used. The mobile phase was 5 mmol/L HNO$_3$ with 3 mmol/L NH$_4$NO$_3$ and 0.75 mmol/L DTPA. The injection volume was 20 µL and the pump flow rate was set at 1.5 mL/min. Limit of detection (LOD), defined as the minimum measured concentration distinguishable from blank, as low as 0.05 µg·L$^{-1}$ was achieved for Tl(I) and Tl(III)-DTPA.

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

The presence of Fe(II) in samples and standard solutions was spectrophotometrically detected by complexation with TPTZ following the procedure of Krishnamurti and Huang (Krishnamurti and Huang, 1990). Briefly, 1.4 mL of sample was added to 0.1 mL of hydrochloric acid (6 mol/L). Then, 0.2 mL of NH$_4$F (2 mol/L), 0.2 mL of TPTZ (2.4 mmol/L in 0.12 mol/L HCl), and 0.4 mL of ammonium acetate buffer (2 mol/L, pH 4.5), were added in this order. The presence of iron(II) is indicated by the formation of the intense violet complex (λ$_{max}$ 597 nm).

3. Results
3.1 Characterization of AMD and water sample from Baccatoio stream

The content of total thallium in the collected AMD and in stream water samples, determined by ICP-MS, was 948±42 µg/L and 153±5 µg/L, respectively.

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

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

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

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

The effect of pH on Tl(I) oxidation was evaluated by increasing the pH of AMD from 2.1 to 3.3 with saturated sodium carbonate. After increasing the pH, the sample was exposed to sunlight and also in this case almost 80 % Tl(III) with respect total thallium was detected (Figure 3).
Figure 3. Percentage of Tl(III) respect to total thallium found by IC-ICP-MS in not filtered samples exposed for 8 h to sunlight (white bars), followed by 12 h (grey bars) and 5 d (spotted bars) in the dark. Errors are reported as relative standard deviation calculated from 3 repeated measures.

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

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

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

In the synthetic solution, a comparable extent of Tl(I) → Tl(III) oxidation was obtained after the exposure to sunlight or UV irradiation (Figure 6). However, the reduction of Tl(III) to Tl(I) proceeded faster compared with natural samples (see Figure 3 and 4), and after 12 h in the dark less than 3% Tl(III) persisted in solution.
Figure 6. Percentage of Tl(III) respect to total thallium found by IC-ICP-MS in Tl(I)-Fe(III) standard 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: sunlight; grey bars: UV light). Errors are reported as relative standard deviation calculated from 3 repeated measures.

Unlike what we observed in natural samples, no oxidation of Tl(I) to Tl(III) occurred when the standard solution was exposed to 12 h LED irradiation. Thus, it is argued that in natural waters more chemical species, other than Fe(III)/Fe(II), are involved in Tl(I) oxidation. Under light illumination, electrons might be transferred from Tl(I) to Fe(III) through a ligand-to-metal charge-transfer process, which could be greatly influenced by the type of ligands coordinated to Fe(III). It is reported that over 99% of dissolved iron may be complexed to organic matter in natural waters, greatly increasing the solubility of iron and preventing the precipitation of oxyhydroxides (Su et al., 2015). Iron(III) organic complexes, such as Fe-oxalate, Fe-citrate and Fe–fulvic acid (the fraction of humic acids soluble at low pH) can be photolyzed to generate reactive species, such as $O_2^-$, $H_2O_2$, $\cdot OH$ (Kong and He, 2016). Thus, we separately added to the Tl(I)+Fe(III) synthetic solution these three organic compounds: citric (1 mmol/L), oxalic (1 mmol/L) and fulvic acid (10 mg/L). Irradiation experiments with LED were repeated, revealing that only the addition of soil fulvic acid produced a signal of Tl(III) significantly different from the blank (5.6 µg/L, corresponding to the...
0.9 % of total thallium). However, the signal intensity was not sufficient to justify the almost quantitative oxidation observed in natural samples.

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

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

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

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

### 3.3 Tl redox state and reactivity in pipelines

A source of Tl contamination, directly related to the human exposure (Campanella et al., 2016), was found in the crust deposited in the pipeline of the aqueduct system of the Valdicastello Carducci village. Crust samples were scraped from two pipeline segments removed from the drinking water distribution system, respectively before and after a disinfection system.
Total thallium analysis by microwave digestion with nitric acid/H$_2$O$_2$ and ICP-MS gave 0.31 and 42.5 mg/g of thallium in the pre- and post-water treatment pipeline, respectively. The recovery of total thallium after leaching with 5 mmol/L DTPA + 2 wt% HNO$_3$ was 98.2% (0.30 mg/g) and 92.7% (39.4 mg/g), respectively.

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

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

Three oxidants commonly used in water treatment systems, i.e. sodium hypochlorite and hydrogen peroxide with or without acetic acid, were tested to evaluate their effect on thallium speciation in rust scale. The amount of thallium in solution with respect to leaching in water decreased after treatment with 0.16 mol/L NaClO down to 4.3% (0.013 mg/g) and 6.3% (2.6 mg/g) with respect total thallium measured after microwave digestion. In addition Tl(III) was not detected in solution.

On the other hand, treatment with 1.5 wt% H$_2$O$_2$ or 1.5 wt% H$_2$O$_2$ + 0.5 wt% acetic acid (acetic acid was added to mimic the use of peracetic acid, another common disinfectant), with respect to leaching in water, increased the percentage of total thallium in solution up to 21.7% (0.067 mg/g) and 72% (28.5 mg/g) in the pre- and post-water treatment pipeline, respectively. However these treatments did not influence the thallium speciation.
Table 1. Results from leaching experiments on 100 mg pipeline rust in 5 mL solution (pre = pipeline removed before the water treatment plant; post = pipeline removed after the water treatment plant).

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

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

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

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

The treatment with 0.16 mol/L NaClO was replicated on a sample collected from the thallium-contaminated water spring that until 2014 has been used to feed the public aqueduct of Valdicastello. The concentration of total thallium in this sample was 11.5 µg/L (±0.3 µg/L), and from IC-ICP-MS analysis it resulted composed only by Tl(I). The treatment with H₂O₂ or H₂O₂/acetic acid did not influence thallium speciation. After the addition of NaClO, the analysis of
the sample filtered (through 0.22 µm membrane filter) and treated with DTPA+HNO₃ showed thallium levels below the detection limit of the method. The analysis of the same sample, firstly treated with DTPA+HNO₃ and successively filtered, revealed the presence of Tl(III) with a conversion yield of 94.8% with respect to original Tl(I).

4. Discussion

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

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

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

Oldenburg and co-workers (1997) and Horváth and co-workers (1999) studied the photochemical reaction mechanism of thallium in strongly alkaline solution by irradiating TiClO₄ in 1 mol/L
NaOH solution using a high pressure UV light. The irradiated solution yielded a yellow-brown suspension, and the same result was obtained by Li and co-workers in neutral solutions (2005). Karlsson and co-workers. (2006) also verified that UV light produced Tl(III) in standard solutions of Tl(I) and Fe(III).

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

The detection of Fe(II) even in a synthetic solution composed only of Fe(III) in 5 mmol/L H$_2$SO$_4$, after irradiation with UV and solar light indicated that there is not a direct electron transfer between iron and thallium. It is known, indeed, that in aqueous solutions Fe(III) alone undergoes cyclic photochemical reduction to Fe(II) when irradiated with UV light (Feng and Nansheng, 2000).

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

A connection between environmental threats and waterborne human diseases has been since long recognized (e.g. McMichael, 1994). In the case of the past-mining impacted Baccatoio basin, Biagioni and co-workers (2017) recently found solid Tl(III) and Tl(I)-phases represented by Tl$_2$O$_3$ and TlCl in rust scales from pipelines of the Valdicastello Carducci waterwork, since long fed by Tl(I)-contaminated waters. They attributed the Tl(I) oxidation and Tl$_2$O$_3$ particle precipitation to water chlorination in a treatment plant. Our results confirm this hypothesis.
A series of leaching experiments were performed on rust scales removed from pipeline segments taken before and after the Valdicastello Carducci public water-treatment plant, with the aim to evaluate i) how much thallium contained in the scales may dissolve into water, ii) which is the form of soluble thallium and iii) thallium reactivity. The results indicated that a minor but significant fraction of thallium is released from scales to both deionized and tap waters, in the sole form of Tl(I), and that the amount is higher in the pipeline after the treatment plant. This thallium likely originated from Tl(I) chloride dissolution \( (K_{sp} = 10^{-3.65}) \) (Xiong, 2009), in agreement with the observation that Tl(III) oxide is rather insoluble in water \( (K_{sp} = 10^{-5.8} \text{ mol/L at pH 7 and } 10^{-11.7} \text{ mol/L at pH 9}) \) (Nagy et al., 2005; Xiong, 2009). From the data of Schindler (1958) the solubility product of \( \text{Tl}_2\text{O}_3 \) for the reaction \( \text{Tl}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Tl}^{3+} + 3\text{H}_2\text{O} \) in 3.5 mol/L NaClO₄ is \( K_{sp} = 10^{-2.34}, \) and the solubility equilibrium may be further altered if complexing agents are present in solution.

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

5. Conclusion

To date, literature cannot explain the behaviour of thallium and its speciation in the aqueous media and in even more complex natural systems. The difficulties in reconciling thermodynamic...
predictions and speciation analytical data are confirmed in our previous work, where we reported the finding of Tl(III) in natural waters (Campanella et al., 2017). This paper can be considered as a step forward in the comprehension of Tl(I) and Tl(III) behaviour in real contaminated systems. In summary, we demonstrated that the concentration and thus the distribution of Tl(I) and Tl(III) is affected by radiation and aqueous Fe(III). In absence of Fe(III), no oxidation takes place. In the acid conditions (pH around 2) of both AMD and surface water samples, Tl(III) remained in solution or formed nanoparticulate with dimension less than 200 nm. The oxidation process was reversible, and the reduction showed a slower kinetics in real samples respect to model standard solutions.

When a solution of Tl(I) was irradiated with a LED source, which emits at the boundaries of the UV spectrum (378 nm), Fe(III) was not sufficient to promote the oxidation and the presence of other elements (e.g. arsenic(V) was investigated in this work) is necessary.

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

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