



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



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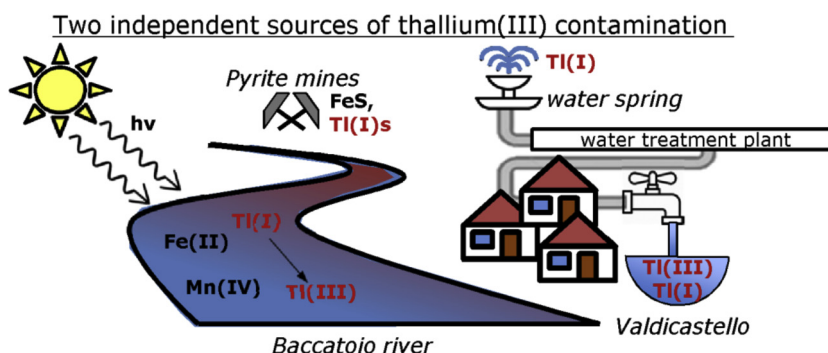
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## HIGHLIGHTS

- Thallium (III) has been found in considerable amounts in tap and surface water.
- UV promotes oxidation of Tl(I) to Tl(III) in standard solutions and real samples.
- LED at 379 nm oxidised efficiently Tl(I) only in AMD and surface water.
- Chlorine-based oxidants promote the quantitative conversion of Tl(I) to Tl(III).
- The results can be helpful to better understand Tl mobility and behaviour.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

Article history:

Handling Editor: Martine Leermakers

Keywords:

Thallium  
Tl-bearing pyrite  
Natural waters  
AMD  
Photochemistry  
Oxidation

## 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.

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## 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 behaviour 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<sup>+</sup> is similar to potassium, so it is able to replace the latter during enzymatic reactions. Tl<sup>3+</sup> induces an oxidative stress status in human cells and it was found to be considerably more toxic than Tl<sup>+</sup> 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<sub>4</sub><sup>-</sup> or Cl<sub>2</sub>, 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; Zafriou 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 (Blough and Zepp, 1995). 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<sup>®</sup> nitric acid (HNO<sub>3</sub>, 69%), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, ACS reagent 95–98%) iridium (analytical standard, 1000 mg/L Ir in 10 wt % HCl), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub> 99.999% trace metals basis), diethylenetriaminepentaacetic acid (DTPA), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), acetic acid, sodium hypochlorite (NaClO, available chlorine 10–15%), ammonium fluoride (NH<sub>4</sub>F), and manganese (IV) oxide (MnO<sub>2</sub> 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 HNO<sub>3</sub> (Merck) in the eluent phase. Standard solution of Tl(III) was prepared dissolving Tl(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O (Sigma-Aldrich) in 5 mmol/L HNO<sub>3</sub> – 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

Fig. 1 shows the area object of the study, located in the north-west 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).

### 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<sup>®</sup>, Nalge Nunc International, Rochester, USA) filled to the top (50 mL). For each sample, to one aliquot DTPA (5 mmol/L) with HNO<sub>3</sub> (0.2 mol/L) was added in situ.

In order to gain insights on the formation of Tl(III) in AMD water

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