



# Thallium release from acid mine drainages: Speciation in river and tap water from Valdicastello mining district (northwest Tuscany)



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## ABSTRACT

In this work we present an advantageous method for the simultaneous separation and detection of Tl(I) and Tl(III) species through ion chromatography coupled with on-line inductively coupled plasma – mass spectrometry. Chromatographic separation between Tl(III) and Tl(I) was achieved in less than two minutes. The method was validated by recovery experiments on real samples, and by comparing the sum of the concentrations of individual Tl species with total thallium values obtained from continuous flow ICP-MS. The experimental procedure offers an accurate, sensitive and interference-free method for Tl speciation at trace levels in environmental samples. This allowed us to investigate the Tl speciation in acid mine drainages (AMD), surface waters and springs in a mining catchment in Valdicastello Carducci (Tuscany, Italy), where severe Tl contamination had been evidenced previously. This study shows for the first time that Tl(III), in addition to Tl(I), is present in considerable amounts in water samples affected by acid mining outflow, raising the question of the origin of this thermodynamically unstable species.

## 1. Introduction

In the last years an increasing attention has been paid to thallium (Tl) speciation, as it affects the toxicity and distribution of this metal. Currently, chronic intoxication by Tl seems to be a global phenomenon, as several cases of water contamination have been registered [1–5]. Recently, the European COST Action TD1407 action included Tl in the list of technology-critical elements, with associated environmental impact and potential human health threats [6]. Thallium is a cumulative poison, and symptoms of Tl intoxication include nausea, vomiting, abdominal pain, hair loss, alopecia, tachycardia and cardiac arrhythmias. It is also a neurotoxin which causes tremor, ataxia, ptosis of the eyelids, painful lower extremities, paresthesias of hands and feet after a few days of intoxication. The well-known mechanism of Tl toxicity is related to the interference with the vital potassium-dependent processes, substitution of potassium in the (Na<sup>+</sup>/K<sup>+</sup>)-ATPase, as well as a high affinity for sulfhydryl groups from proteins and other biomolecules [7].

U.S. EPA fixed the maximum contaminant level of Tl in drinking

water at 2 µg L<sup>-1</sup> with the goal of lowering it at 0.5 µg L<sup>-1</sup> [8]. The maximum concentration level of Tl in tap water is regulated by several guidelines also in other countries, such as China [9], Canada [10], Mexico and Latin America [11], and Russia [12]. In Italy, Tl concentration is regulated only in wastewaters and groundwaters (maximum level fixed at 1 µg L<sup>-1</sup> and 2 µg L<sup>-1</sup>, respectively) [13,14].

Acid mine drainages (AMD), which are responsible for the releasing of toxic elements to the environment, represent a common legacy of past-mining activity. Whereas some metals, such as Fe, Al, As and Cu are readily scavenged from the aqueous phase as pH increases, others such as Sb, Cd, Zn, and Tl may remain partly in solution [15–17], thus threatening freshwater resources, including those used for drinking water supply.

Thallium has two oxidation states, Tl(I) and Tl(III), with different properties and toxicity. An exhaustive review [18] highlights the differences in terms of bioaccumulation and toxicity of both Tl species in aquatic systems. These differences draw further attention to the importance of speciation studies of Tl.

Compared with Tl(III), Tl(I) is thermodynamically more stable in aqueous solution over a wide pH range, including the conditions of

*Abbreviations:* AMD, acid mine drainages; BC, Baccatoio creek; BC<sub>OLD</sub>, Baccatoio creek old samples DTPA: diethylenetriaminepentaacetic acid; EPA, Environmental Protection Agency; IC-ICP-MS, ion chromatography – inductively coupled plasma – mass spectrometry; Tl, thallium; TW, tap water

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most natural waters. In aquatic environments, dissolved thallium is expected to be present mostly as Tl(I) free ionic form [19], except in the case of saline waters where chloride and sulfate may be important ligands. Thallium(III) is indeed subject to both spontaneous reduction to Tl(I) ( $E_{h(Tl^{3+}/Tl^+)} = +1.26$  V) and precipitation as  $Tl(OH)_3$  at  $pH < 7$  ( $K_{sp_{25}^{\circ}C} = 1.68 \cdot 10^{-44}$ ). The occurrence of stable trivalent form in solution is possible at higher pH, where hydroxide complexes are formed [20], and in the presence of ligands such as chlorides ( $\log \beta [TlCl_4^-] = 17$ ) or acetate ( $\log \beta [Tl(CH_3CO_2)_4^-] = 15.4$ ) [21]. To prevent the reduction and hydrolysis of Tl(III), diethylenetriaminepentaacetic acid (DTPA) can be added to the sample. The Tl(III)-DTPA complex is indeed very stable ( $\log \beta [Tl(III)-DTPA] = 46$ ) [22], while DTPA does not complex Tl(I).

A number of techniques have been published for the speciation of Tl at ultratrace levels in natural waters [19,23–27]. Among these, ion exchange chromatography (IC) with on-line inductively coupled plasma – mass spectrometry (ICP-MS) detection appeared as the most promising technique for speciation analysis of Tl using complexation with DTPA to separate Tl(III)-DTPA from  $Tl^+$  [12,28–34]. Most of these methods used anion exchange chromatography and suffered a long analysis time while fastest methods that used cation exchange chromatography have never been applied to complex matrices such as mine waters.

In this study we describe a fast, sensitive and reliable method for the redox speciation of Tl in water, based on cation exchange chromatography coupled to ICP-MS detection. After its optimization, the method was applied to the determination of Tl species in water samples collected from the Tl-contaminated area in the abandoned mining site of Valdicastello Carducci (Tuscany, Italy).

The influence of the sampling procedure on Tl speciation is also here discussed. Considering the unique nature of the analysed samples, some speculations about the Tl geochemical behaviour are also reported.

## 2. Materials and methods

### 2.1. Reagents

High purity water (18.2 M $\Omega$ -cm) was obtained with an Elga Purelab-UV system (Veolia Environment, Paris, France). TraceCERT®  $HNO_3$  (69%), iridium (analytical standard, 1000  $\mu g mL^{-1}$  Ir in 10 wt% HCl), ammonium acetate (99.999% trace metals basis), and DTPA were purchased from Sigma-Aldrich. Standard solutions of Tl(I) were prepared by dilution of 1000  $mg L^{-1}$  Tl in 0.5  $mmol L^{-1}$   $HNO_3$  (Merck) in the eluent phase. Standard solution of Tl(III) was prepared dissolving  $Tl(NO_3)_3 \cdot 3H_2O$  (Sigma-Aldrich) in 5  $mmol L^{-1}$   $HNO_3$  – 5  $mmol L^{-1}$  DTPA. Water certified reference material (NIST1640A) was obtained from NIST (National Institute of Standard Technology, USA).

### 2.2. Site description

Fig. 1 shows the area object of the study, located in the northwest of Tuscany (Italy), together with the sampling stations. The main subject of the study is the Baccatoio creek, which is about 11 km long and has a 26.7  $km^2$  catchment area. The Baccatoio creek receives some tributaries and spring waters from its catchment area and also various AMD that discharge from the dismissed tunnels directly into the creek. It

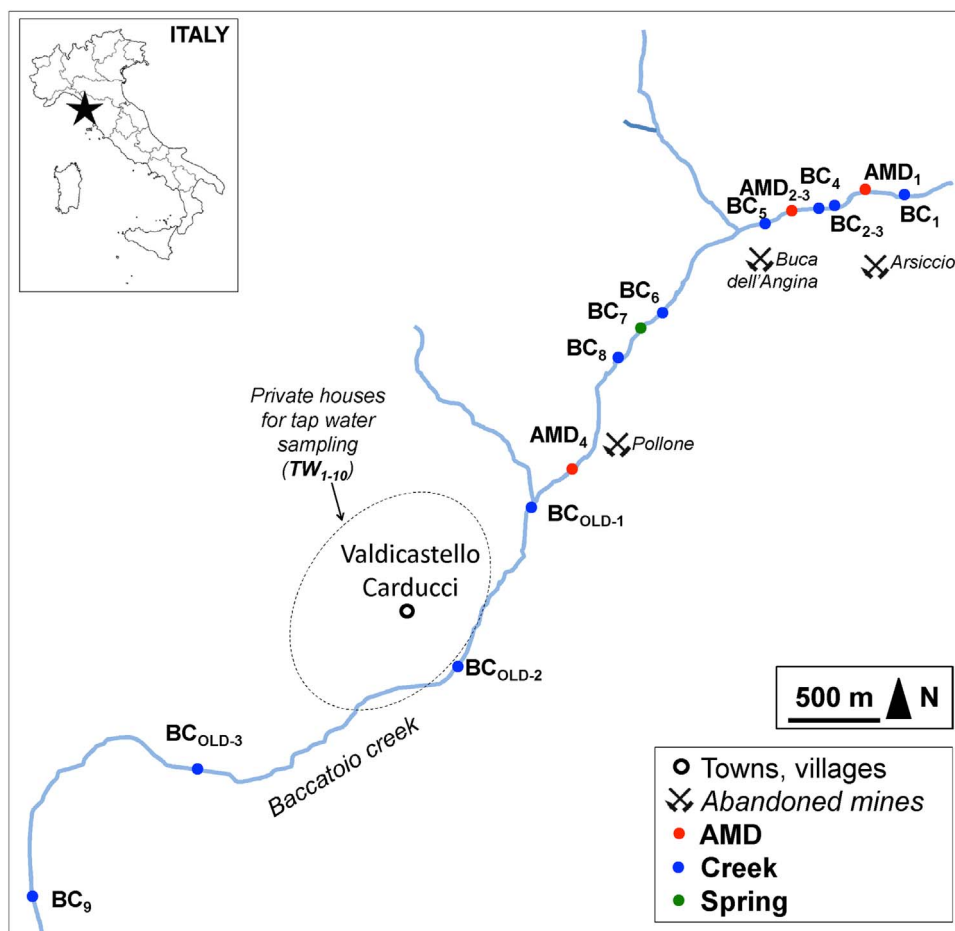


Fig. 1. Sketch map showing the localities cited in the text, the water system of the Baccatoio creek and the sampling sites (AMD<sub>x</sub>: acid mine drainage; TW<sub>x</sub>: tap water; BC<sub>x</sub>: Baccatoio creek).

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