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Predominance of Aqueous Tl(I) Species in the River System Downstream from the Abandoned Carnoulès Mine (Southern France)

Corinne Casiot,^{*,†} Marion Egal,[†] Odile Bruneel,[†] Neelam Verma,[†] Marc Parmentier,[‡] and Françoise Elbaz-Poulichet[†]

[†]HydroSciences UMR 5569 CNRS - Universités Montpellier I and II – IRD, Place Eugène Bataillon, CC MSE, 34095 Montpellier cedex 5, France

[‡]BRGM, service Eau/M2H, 3 avenue Claude Guillemin, BP 36009, 45060 Orléans Cedex 2, France

ABSTRACT: Thallium concentration reached up to $534 \mu\text{g L}^{-1}$ in the Reigous acid mine drainage downstream from the abandoned Pb–Zn Carnoulès mine (Southern France). It decreased to $5.44 \mu\text{g L}^{-1}$ in the Amous River into which the Reigous creek flows. Tl(I) predominated (>98% of total dissolved Tl) over Tl(III), mainly in the form of Tl^+ . Small amounts of Tl(III) evidenced in Reigous Creek might be in the form of aqueous TlCl_2^+ . The range of dissolved to particulate distribution coefficients $\log K_d = 2.5 \text{ L kg}^{-1}$ to 4.6 L kg^{-1} indicated low affinity of Tl for particles, mainly ferrihydrite, formed in the AMD-impacted watershed. The low retention of Tl^+ on ferrihydrite was demonstrated in sorption experiments, the best fit between experimental and modeled data being achieved for surface complexation constants $\log K_{\text{ads}} = -2.67$ for strong sites and $\log K_{\text{ads}} = -3.76$ for weak sites. This new set of constants allowed reasonable prediction of the concentrations of aqueous and particulate Tl resulting from the mixing of water from Reigous Creek and the Amous River water during laboratory experiments, together with those measured in the Amous River field study.

INTRODUCTION

Thallium is present at trace levels in the environment, at concentrations of $5\text{--}10 \text{ ng L}^{-1}$ in freshwaters,¹ and of $0.08\text{--}1.5 \text{ mg kg}^{-1}$ in soils.² However, its toxicity to mammals is similar to that of Hg, Cd, or Pb, and the nondiscriminatory uptake of Tl^+ over K^+ has been suggested as a mechanism for its detrimental effect to biota, for example during Na K-ATPase synthesis.³ Tl occurs at relatively high concentrations in sulfide ores (e.g., pyrite), whereas it is seldom recovered from metal-based mining, ore processing, or smelting operations and is generally discarded as part of the tailings.⁴ It results in considerable Tl enrichment of soils and water around mining sites.^{2,5–7} Tl can enter the terrestrial food-chains as demonstrated by the 3- and 10-fold increase in its concentration respectively in liver and kidney of shrews from the Doñana national park (southwest Spain) after the collapse of the Aznalcollar mine tailing.⁸ Thallium has two oxidation states, monovalent Tl(I) and trivalent Tl(III), which differ in terms of toxicity and chemical reactivity. Tl(III) was reported to be approximately 50000-fold more toxic for the unicellular chlorophyte *Chlorella* than Tl(I).⁹ Tl(I) should dominate in oxic waters, due to the high redox potential of Tl(III)/Tl(I) couple ($E_h = 1.28 \text{ V}$). Furthermore, Tl(III) forms hydroxo-complexes with low solubility (from $10^{-5.8} \text{ mol L}^{-1}$ at pH 7 to $10^{-11.7} \text{ mol L}^{-1}$ at pH 9 at $E_h 0.55 \text{ V}$),¹⁰ which limits the concentration of Tl(III) in solution. However, measurements of Tl speciation in natural waters contradict thermodynamic predictions. In seawater, 80% of thallium is in the oxidized form Tl(III), because this redox state is stabilized as an anionic complex with Cl^- or OH^- .¹¹ In the Great Lakes, Lin and Nriagu¹² also found that Tl(III) was predominant ($68 \pm 6\%$ of total dissolved Tl) despite thermodynamic predictions. These results were first contested¹³ but finally confirmed by Twining et al.¹⁴ who demonstrated that this thermodynamic disequilibrium was related to

bacterial activity; indeed, these authors showed that microorganisms originating from lake and pond waters oxidize Tl(I) into Tl(III) which is believed to be subsequently stabilized by complexation with organic or inorganic substances or formation of dimethylthallium.¹⁴ Oxidation of Tl(I) can also take place when it is exposed to UV irradiation or sunlight.^{15,16}

Knowledge of Tl speciation is of primary importance to evaluate the mobility of Tl in the environment. The geochemical behavior of Tl(I) is very similar to that of K^+ , showing great mobility in soils and natural waters.^{17,18} Mn-oxides are able to trap Tl(I), but the mechanism appears to involve oxidation of Tl(I) into Tl(III) and precipitation of Tl_2O_3 at the surface of the oxide.¹⁹ Fe-sulfides have been suggested to sequester Tl(I) in anoxic lake sediments.²⁰ In acid mine waters enriched with aluminum and sulfate, Tl(I) precipitated in the form of lanmuchangite $\text{TlAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.¹⁰ Conversely, Tl(III) presents a high affinity for Fe and Mn oxyhydroxydes.^{19,21} Furthermore, Tl(III) hydroxides have low solubility in the absence of ligands. These properties limit the mobility of this species.

Despite its high toxicity, relatively little attention has been paid to Tl behavior in freshwater environments. The aim of this study was to investigate the behavior of Tl in surface waters affected by acid mine drainage (AMD) from the abandoned Pb–Zn mine of Carnoulès (southern France). Concentrations of Tl were monitored along a 9-km river transect downstream from the mine with emphasis on speciation and distribution between aqueous and solid phases throughout the hydrosystem. Laboratory experiments were

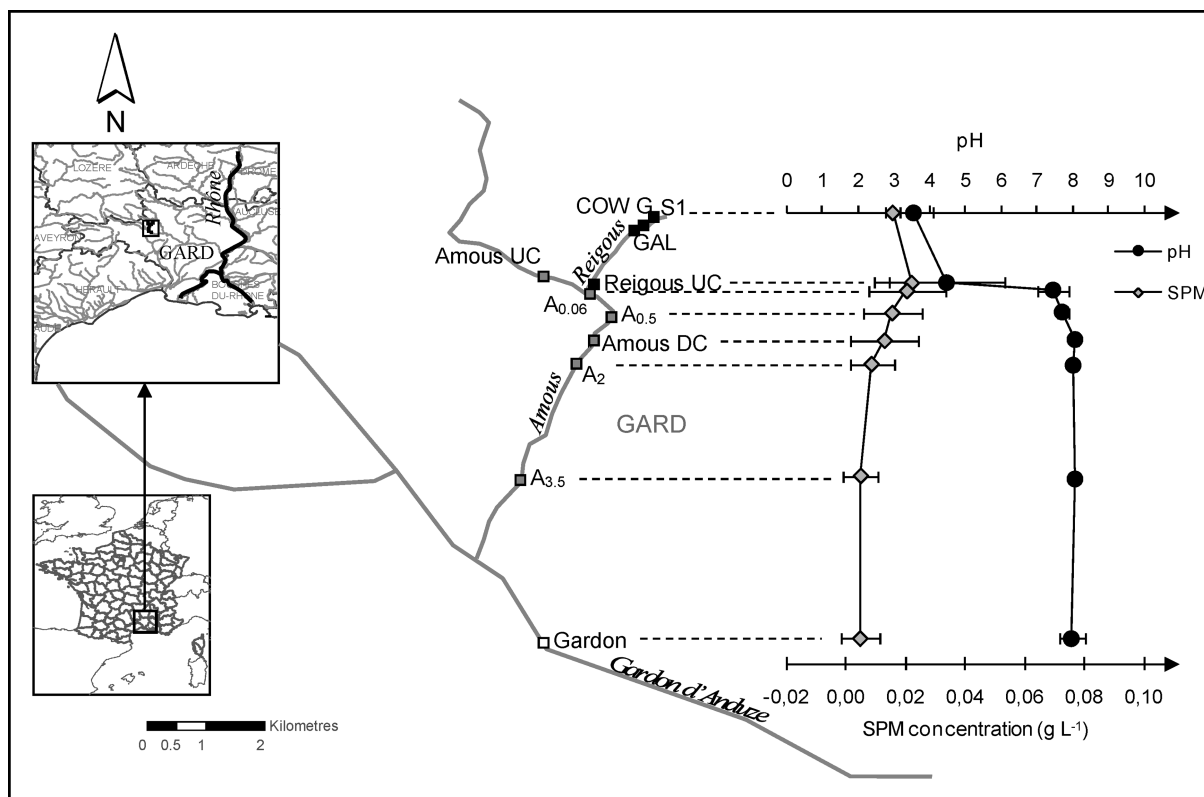


Figure 1. Sketch map of the study area with location of the sampling points along the watershed and variations in the average pH and suspended particulate matter (SPM) concentrations from data collected during the 2002–2003 survey.

carried out to better understand the processes that control Tl behavior.

EXPERIMENTAL SECTION

Site Description. Carnoulès mine is located in southern France in the drainage basin of the Rhône River (Figure 1). Mining activity stopped in 1962 but left about 1.5 Mt of sulfidic wastes containing 0.7% Pb, 10% Fe, 0.2% As, and 13 to 40 $\mu\text{g Tl g}^{-1}$ (dry weight) deposited over a segment of the Reigous Creek.²² The origin of thallium in the Pb–Zn deposits from the Cévennes border in France has been investigated by Duchesne.²³ A geochemical study of Fe-sulfides (pyrite and marcasite) associated with Pb–Zn vein deposits showed the presence of relatively large amounts of thallium (300 to 1500 mg kg^{-1}). These high concentrations may be related, according to this author, to the influence of epithermal solutions. At Carnoulès, the subsurface waters draining the tailings impoundment emerge at the base of a dam and form the spring of Reigous Creek. The water is limpid, slightly oxygenated ($\text{DO} \sim 0.2 \text{ mg/L}$), acid ($\text{pH} \sim 3\text{--}4.5$) and contains Fe ($\sim 2 \text{ g L}^{-1}$), sulfate ($\sim 4 \text{ g L}^{-1}$), and arsenic (250 mg L^{-1}) at extremely high concentrations. Heavy metals, such as Pb and Zn, are also present. Reigous Creek also collects acidic seepage waters from the surrounding quarries. It joins the Amous River 1.5 km downstream from its source. At the confluence with the Amous River (Figure 1), the Reigous discharge ranges between 0.6 and 20 L s^{-1} . The Amous discharge ranges between 50 and 150 L s^{-1} . Upstream from the confluence, the Amous River is not affected by AMD, and the concentrations of dissolved metals, arsenic and sulfate, which are generally several orders of magnitude lower than in Reigous Creek, provide no evidence of contamination but simply reflect the natural regional background.²⁴ The mixing of the alkaline

waters of the Amous River and the acidic waters of Reigous Creek increases the pH downstream (Figure 1) and causes the precipitation of Fe and Al (ferrihydrite and gibbsite). This suspended particulate matter (SPM) removes most metals from the dissolved phase.²⁴

Sample Collection and Processing. Water samples were collected during 63 surveys. The location of sampling stations along the 9-km transect from the source of the Reigous Creek to the Gardon River is shown in Figure 1. The Amous UC station located on the Amous River 1500 m upstream from the confluence with Reigous Creek is not affected by the presence of mineralization or former mining activities.

Nine surveys were carried out from June 2002 to November 2003; they were focused on the Amous River which receives the AMD input directly and the Gardon River downstream from the confluence with the Amous River. The aim of these campaigns was to establish the levels of thallium along the watershed. During this period, one station (Reigous UC) located on Reigous Creek a few meters upstream from the confluence with the Amous River was also monitored to assess the metal input from the tailings impoundment. During the 54 following surveys from November 2004 to October 2008, sampling focused on Reigous Creek, to better assess the behavior of Tl in the acid water. During this period, only one station (Amous DC) on the Amous River was monitored; this station was located 1.2 km downstream from the confluence with Reigous Creek. Water samples for ultrafiltration and redox Tl speciation were collected respectively in March and October 2008.

The pH and redox potential were measured in the field with an Ultrameter Model 6P (Myron L Company, Camlab, Cambridge). pH measurements were made using a glass–Ag/AgCl reference electrode couple calibrated with two standard buffer solutions ($\text{pH} = 4.005$ and $\text{pH} = 7.000$, Hach Lange France) traceable to

Table 1. Relevant Redox, Complexation, and Solubility Equilibrium Constants for Thallium Used in the Calculations

reaction	log K (25 °C)	reference
$Tl^+ + SO_4^{2-} = TlSO_4^-$	1.37	20
$Tl^+ + Cl^- = TlCl(aq)$	0.51	20
$Tl^+ + 2Cl^- = TlCl_2^-$	0.28	20
$Tl^+ + H_2O = TlOH(aq) + H^+$	-13.207	20
$Tl^+ + CO_3^{2-} = TlCO_3^-$	2.16	27
$Tl^+ + 2CO_3^{2-} = Tl(CO_3)_2^{3-}$	0.11	20
$Tl^+ + HCO_3^- = TlHCO_3$	0.9	27
$Tl^+ + HS^- = TlHS(aq)$	2.27	20
$2Tl^+ + HS^- = Tl_2HS^+$	8.04	20
$2Tl^+ + 2H_2O + 2HS^- = Tl_2(OH)_2(HS)_2^{2-} + 2H^+$	-11.068	20
$2Tl^+ + H_2O + 3HS^- = Tl_2OH(HS)_3^{2-} + H^+$	1.004	20
$Tl^+ + Ful1^- = Tl-Ful1$	4.83	30
$Tl^+ + Ful2^- = Tl-Ful2$	3.32	30
$>HFO(s)-OH + Tl^+ = >HFO(s)-OTl + H^+$	-2.69	this study
$>HFO(w)-OH + Tl^+ = >HFO(w)-OTl + H^+$	-3.76	this study
$Tl^+ + 0.5 H_2O = Tl(s) + H^+ + 0.25O_2$	-27.1743	29
$2Tl^+ + CO_3^{2-} = Tl_2CO_3(s)$	3.837	20
$Tl^+ + H_2O = TlOH(s) + H^+$	-12.919	20
$2Tl^+ + H_2O = Tl_2O(s) + 2H^+$	-27.091	20
$2Tl^+ + SO_4^{2-} = Tl_2SO_4(s)$	3.787	20
$2Tl^+ + HS^- = Tl_2S(s) + H^+$	7.19	20
$Tl^+ + 2SO_4^{2-} + 3Fe^{3+} + 6H_2O = TlFe_3(SO_4)_2(OH)_6(s) + 6H^+$	2.245	^a
$Tl^+ + Al^{3+} + 2SO_4^{2-} + 12H_2O = TlAl(SO_4)_2 \cdot 12H_2O(s)$	16.551	^a
$Tl^+ + H_2AsO_3^- + 2HS^- + 2H^+ = TlAsS_2(s) + 3H_2O$	38.256	^a
$Tl^+ + 2H^+ + 0.5O_2 = Tl^{3+} + H_2O$	-0.2751	29
$Tl^{3+} + 3H_2O = Tl(OH)_3(aq) + 3H^+$	-3.291	20
$Tl^{3+} + 3H_2O = Tl(OH)_3(s) + 3H^+$	2.15	20
$Tl^{3+} + H_2O = TlOH^{2+} + H^+$	-0.597	20
$Tl^{3+} + 2H_2O = Tl(OH)_2^+ + 2H^+$	-1.394	20
$Tl^{3+} + 4H_2O = Tl(OH)_4^+ + 4H^+$	-14.988	20
$Tl^{3+} + Cl^- + H_2O = TlOHCl^+ + H^+$	7.338	20
$2Tl(OH)_3(aq) = Tl_2O_3(s) + 3H_2O$	16.3237	28
$Tl^{3+} + Cl^- = TlCl^{2+}$	7.72	20
$Tl^{3+} + 2Cl^- = TlCl_2^+$	13.48	20
$Tl^{3+} + 3Cl^- = TlCl_3(aq)$	16.5	20
$Tl^{3+} + 4Cl^- = TlCl_4^-$	18.3	20
$Tl^{3+} + SO_4^{2-} = TlSO_4^+$	1.929	20
$Tl^{3+} + 2SO_4^{2-} = Tl(SO_4)_2^-$	3.719	20
$Tl^{3+} + SO_4^{2-} + H^+ = TlHSO_4^{2+}$	3.129	20
$Tl^{3+} + 2SO_4^{2-} + 2H^+ = Tl(HSO_4)_2^{2+}$	5.939	20

^a Calculated according to Gibbs free energy of formation from refs 10 and 27.

IUPAC pH scale. Water samples were immediately filtered through 0.22 μ m Millipore membranes fitted on Sartorius polycarbonate filter holders. Samples for the determination of major cations

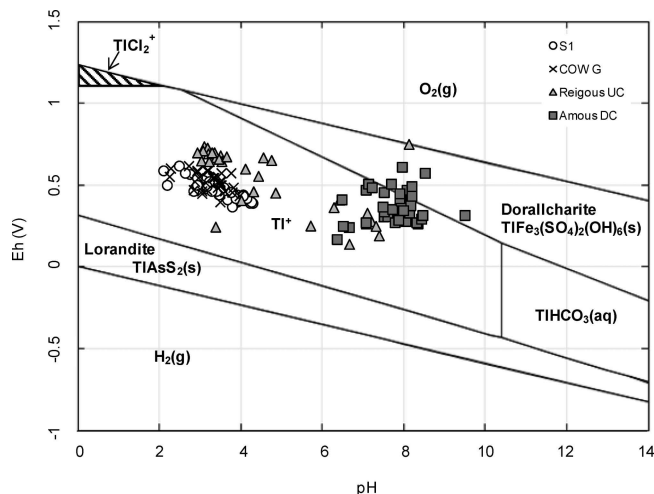


Figure 2. Eh-pH diagram of thallium: concentrations used in the CHES simulation were mean dissolved concentrations at station Amous DC from 17 surveys carried out between 2002 and 2005 (ref 24). The use of concentration values from Reigous UC station lead to a slightly larger stability field for dorallcharite ($TlFe_3(SO_4)_2(OH)_6$) and the replacement of the $TlCl_2^+$ species by $TlCl_3(aq)$. The Tl^+ species was replaced by $TlSO_4^+$ in the diagram for SO_4^{2-} concentrations higher than 4.1 g L^{-1} , which occurred at station S1.³⁶ Hatched area corresponds to area in which Tl(III) predominated; plain areas represent areas in which Tl(I) predominated.

(Ca^{2+} , Na^+ , Mg^{2+}) were acidified to pH = 1 with HNO_3 (14.5 mol L^{-1}) and stored at 4°C in polyethylene bottles until analysis. The samples for the determination of anions (Cl^- , SO_4^{2-}) were frozen on return to the laboratory. For Tl redox speciation analysis, all samples were processed in the field in 100 mmol L^{-1} ammonium acetate and 5 mmol L^{-1} diethylenetriaminepentaacetic acid (DTPA). This solution was used for the extraction of Tl species from plant material;²⁵ indeed, DTPA formed a strong complex $Tl(DTPA)^{2-}$ with Tl(III), enabling stabilization of this species in solution.^{25,26} Furthermore, DTPA also chelated Fe, avoiding possible loss of Tl by adsorption onto Fe oxyhydroxides, which might precipitate at the head of the chromatographic column or during storage. For the S1, COW G and GAL samples, which contained Fe concentrations $\geq 33 \text{ mg L}^{-1}$, only 1 mL of sample was added to 1 mL of preservative solution containing a mixture of 1 mol L^{-1} ammonium acetate and 50 mmol L^{-1} DTPA, and the mixture was completed to 10 mL with deionized water. For samples from Reigous UC, Amous UC, Amous DC, and Gardon stations, which contained Fe concentrations $\leq 10 \text{ mg L}^{-1}$, 1 mL of preservative solution was added to 9 mL of water. Samples were transported to the laboratory immediately after sampling and analyzed within 8 h of collection.

Ultrafiltration experiments were performed using 15 mL centrifugal tubes (Millipore Amicon Ultra-15) equipped with permeable membrane of 10 kDa (with $1 \text{ Da} = 1 \text{ g mol}^{-1}$). Metal-colloid complexes are retained by the ultrafiltration membrane, while free ions and smaller complexes pass into the ultrafiltrate. The degree of metal-colloid complexation is usually determined from the metal concentration in the ultrafiltrate compared to that in the original solution. Each centrifugal filter device was washed and rinsed with HNO_3 0.1 mol L^{-1} , and Milli-Q water before use. Water samples were first filtered using $0.22 \mu\text{m}$ pore size filters. Then an aliquot of the filtrate was passed through the 10 kDa membrane. Centrifugation (3000 g for 30 min and at room temperature) was performed

with a Rotofix 32 (Hettich) centrifuge equipped with a swinging bucket.

The weight of SPM recovered on the 0.22 μm pore size filter was determined after drying in an oven at 105 $^{\circ}\text{C}$ until constant weight. The SPM was then mineralized on a hot plate in concentrated HNO_3 (80 $^{\circ}\text{C}$, 24 h). The amount of trace elements extracted using this one step procedure matched the amount extracted using a three step procedure employing 30% H_2O_2 , then 65% HNO_3 , and finally 40% HF , which was validated

on a standard reference sediment PACS-2 from the NRCC (Ottawa, Ontario, Canada).

Chemical Analyses. An ICS 1000 ion chromatography system (Dionex) was used for the determination of major cation and anion concentrations. Total Fe (dissolved and colloidal) was determined by Flame or Graphite Furnace Atomic Absorption Spectrometry (Thermo Electron Corporation, France). The concentrations of Tl and other trace elements were determined using ICP-MS ("Option S" PQ2+, VG-Elemental, Fisons, and Thermo X7 series). The quality of the analytical methods used was checked by analyzing certified international reference materials: SPS-SW2 batch 119 (Spectra Pure Standards, Promochem, Molsheim, France) and SLRS-4 (NRCC, Ottawa, Ontario, Canada) for concentrations of total Tl and other trace elements in river water, LGC6020 (River Thames, LGC Standards, Molsheim, France) and SLRS-4 for major anions and cations. Accuracy was within 5% of the certified values and the analytical error (relative standard deviation) generally better than 5% for concentrations 10 times higher than the detection limit. Selected samples were analyzed in duplicate, both within the same run and on separate days. These analytical duplicates generally agreed to within $\pm 5\%$.

Redox Tl speciation was carried out by HPLC-ICP-MS. Chromatographic separation was performed using anion-exchange chromatography (15 cm \times 4.1 mm i.d. Hamilton PRP-X100 column with Varian ProStar gradient solvent delivery system) coupled to Thermo X7 Series ICP-MS instrument at a flow rate of 1.5 mL min^{-1} according to a procedure described in Nolan et al.²⁵ The mobile phase used was 100 mmol L^{-1} ammonium acetate buffer (pH 6.2). The standard and samples were prepared in 100 mmol L^{-1} ammonium acetate buffer + 5 mmol L^{-1} DTPA, pH 6.2. A standard solution of Tl(I) (1 g L^{-1}) was prepared by dissolving an appropriate amount of TlNO_3 (Fluka, Buchs, Switzerland) in water. A standard solution of Tl(III) (1 g L^{-1}) was prepared by dissolving an appropriate amount of $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich, Steinheim, Germany) in 100 mmol L^{-1} ammonium acetate buffer and 5 mmol L^{-1} DTPA. The recovery of both Tl species spiked at a concentration of 100 $\mu\text{g L}^{-1}$ in the synthetic mine water sample was checked. For this purpose, 1 mL of synthetic mine water containing 1 g L^{-1} of Fe as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Acros) spiked with either 100 $\mu\text{g L}^{-1}$ of Tl(I) or 100 $\mu\text{g L}^{-1}$ of Tl(III) was added to 1 mL of preservative solution containing a

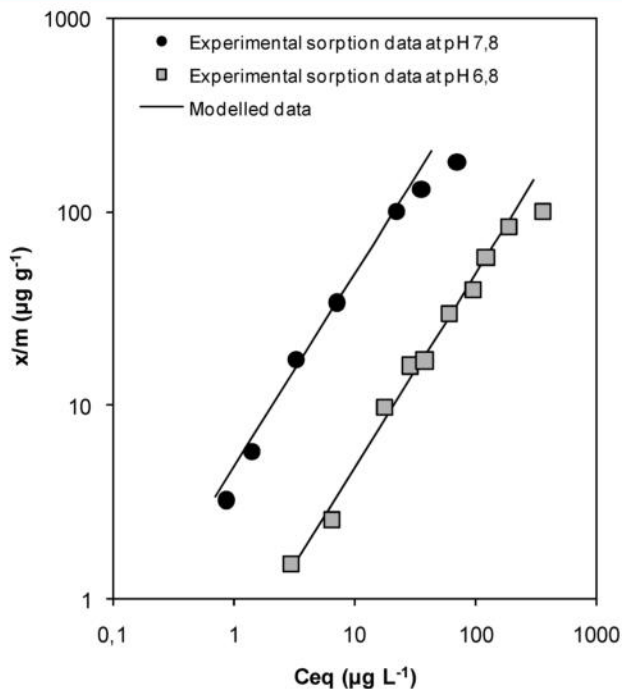


Figure 3. Sorption isotherms of Tl^+ on ferrihydrite at pH 6.8 ± 0.1 and 7.8 ± 0.1 . x/m and C_{eq} represent Tl concentrations in the solid and aqueous phases, respectively. Modeled data were obtained with surface complexation constants of $10^{-2.67}$ for strong sites and $10^{-3.76}$ for weak sites. The volumic density of ferrihydrite (3113.9 kg m^{-3}), radius of particles (10 nm), and surface site densities ($0.093 \mu\text{mol m}^{-2}$ for strong sites, $3.745 \mu\text{mol m}^{-2}$ for weak sites) were CHES default values.

Table 2. Aqueous and Particulate Tl Concentrations ($\mu\text{g L}^{-1}$) at the Sampling Stations along the Watershed Concerned and the Distribution Coefficient ($\log K_d$) between Particulate and Aqueous Tl^a

station	dist. (km)	dissolved phase					particulate phase					
		av	SD	min	max	n	av	SD	min	max	$\log K_d$	n
S1	-1.5	332	82	26	534	51	nd	nd	nd	nd	nd	0
COW G	-1.47	237	71	16	417	47	nd	nd	nd	nd	nd	0
GAL	-1.35	115	60	2	266	48	nd	nd	nd	nd	nd	0
Reigous UC	-0.02	11	8	0.02	51	57	0.2	0.3	0.008	0.84	2.5 ± 0.8 ($n = 7$)	7
Amous UC	-1.5	0.1	0.1	0.01	0.17	23	0.004	0.007	0.0002	0.016	4.5 ± 0.7 ($n = 5$)	5
$A_{0.06}$	0.06	3	2	1.16	5.44	10	0.1	0.1	<DL	0.424	3.1 ± 0.4 ($n = 9$)	9
$A_{0.5}$	0.5	2	1	0.51	3.93	9	0.09	0.09	0.009	0.31	3.4 ± 0.5 ($n = 9$)	9
Amous DC	1.2	0.9	0.5	0.33	2.74	58	0.1	0.3	0.0002	1.8	3.5 ± 0.5 ($n = 8$)	36
A_2	2	0.9	0.5	0.26	2.22	15	0.06	0.07	0.003	0.20	3.7 ± 0.5 ($n = 9$)	9
$A_{3.5}$	3.5	0.7	0.3	0.05	1.18	21	0.01	0.01	0.002	0.035	3.6 ± 0.4 ($n = 8$)	8
Gardon	7	0.07	0.03	0.03	0.13	9	0.007	0.006	0.0003	0.016	4.6 ± 0.6 ($n = 7$)	7

^a av: average; SD: standard deviation; min: minimum recorded value; max: maximum recorded value; n: number of data; nd: not determined; $\log K_d$: logarithmic value of the ratio of the concentration of Tl in the particulate phase to the concentration of Tl in the dissolved phase.

Table 3. Distribution of the Concentration of Dissolved Tl between the Fraction below 0.22 μm ($[\text{Tl}]_{0.22\mu\text{m}}$) and the Fraction below 10 kDa ($[\text{Tl}]_{10\text{ kDa}}$) in the March 18, 2008 Sampling and Redox Speciation (Tl(I) ($[\text{Tl(I)}]_{0.22\mu\text{m}}$), Tl(III) ($[\text{Tl(III)}]_{0.22\mu\text{m}}$) and total Tl ($[\text{Tl}]_{0.22\mu\text{m}}$) Concentrations) in the Fraction Below 0.22 μm in the October 10, 2008 sampling. All Concentrations in $\mu\text{g L}^{-1}$ ^a

station	18/03/2008				14/10/2008					
	$[\text{Tl}]_{0.22\mu\text{m}}$ ($\mu\text{g L}^{-1}$)		$[\text{Tl}]_{10\text{ kDa}}$ ($\mu\text{g L}^{-1}$)		$[\text{Tl}]_{0.22\mu\text{m}}$ ($\mu\text{g L}^{-1}$)		$[\text{Tl(I)}]_{0.22\mu\text{m}}$ ($\mu\text{g L}^{-1}$)		$[\text{Tl(III)}]_{0.22\mu\text{m}}$ ($\mu\text{g L}^{-1}$)	
	av	SD	av	SD	av	SD	av	SD	av	SD
S1	285	3	284	2	537	15	596	45	2.3	0.1
COW G	190	2	189	1	388	9	390	20	1.64	0.08
GAL	138	1	137	2	230	2	244	12	1.37	0.07
Reigous UC	12.1	0.1	11.9	0.1	6.4	0.2	6.8	0.8	0.13	0.02
Amous UC	nd	nd	nd	nd	0.15	0.01	0.07	0.02	<0.05	<0.05
Amous DC	0.63	0.01	0.56	0.05	0.79	0.03	0.69	0.06	<0.05	<0.05
Gardon	nd	nd	nd	nd	0.06	0.01	0.14	0.03	<0.05	<0.05

^a av: average; SD: standard deviation for three replicates; nd: not determined. Data in italics represent concentrations close to detection limits.

mixture of 1 mol L⁻¹ ammonium acetate and 50 mmol L⁻¹ DTPA, and the mixture was completed to 10 mL with deionized water. The recovery reached 105 ± 5% for Tl(I) and 98 ± 5% for Tl(III), indicating no loss of Tl during the chromatographic separation or redox change. For all the real mine water samples analyzed, the sum of Tl(I) and Tl(III) determined by HPLC-ICP-MS matched the total Tl concentration determined by ICP-MS within ±10%. Detection limits as low as 0.05 $\mu\text{g L}^{-1}$ were reached for Tl(I) and Tl(III) species.

To check the accuracy of the filtration procedure, standard solutions of 1 mg Tl(I) L⁻¹ (TlNO₃ in deionized water) or 1 mg Tl(III) L⁻¹ (TlCl₃·xH₂O in 1% HCl) were filtered successively on 0.22 μm and 10 kDa disk filters and analyzed after 10-fold dilution in 100 mmol L⁻¹ ammonium acetate and 5 mmol L⁻¹ DTPA solution. There were no changes in the original Tl speciation during this treatment.

In order to compare speciation measurements with thermodynamic predictions, an Eh-pH diagram was built using the computer program CHESS with the CHESS thermodynamic database and implementing the set of equilibrium constants for thallium from Laforte et al.,²⁰ Xiong et al.,^{10,27} Allison et al.,²⁸ and van de Lee²⁹ (Table 1). Complexation of Tl(I) with natural organic matter in the form of Tl-fulvate complexes Tl-Ful1 and Tl-Ful2 was involved in the simulation using complexation constants from Kaplan and Mattigod.³⁰ The composition of the water from Amous River ($[\text{Tl}^+] = 0.9 \mu\text{g L}^{-1}$, $[\text{Cl}^-] = 6 \text{ mg L}^{-1}$, $[\text{SO}_4^{2-}] = 76 \text{ mg L}^{-1}$, $[\text{Fe}^{2+}] = 54 \mu\text{g L}^{-1}$, $[\text{Al}^{3+}] = 70 \mu\text{g L}^{-1}$, $[\text{H}_2\text{AsO}_4^-] = 30 \mu\text{g L}^{-1}$, $[\text{CO}_2(\text{g})] = 13.9 \text{ mg L}^{-1}$, $[\text{Ful1}] = 1 \text{ mg L}^{-1}$, $[\text{Ful2}] = 1 \text{ mg L}^{-1}$) and Reigous Creek ($[\text{Tl}^+] = 14 \mu\text{g L}^{-1}$, $[\text{Cl}^-] = 34 \text{ mg L}^{-1}$, $[\text{SO}_4^{2-}] = 840 \text{ mg L}^{-1}$, $[\text{Fe}^{2+}] = 23 \text{ mg L}^{-1}$, $[\text{Al}^{3+}] = 14 \text{ mg L}^{-1}$, $[\text{H}_2\text{AsO}_4^-] = 1000 \mu\text{g L}^{-1}$, $[\text{CO}_2(\text{g})] = 13.9 \text{ mg L}^{-1}$) used in the CHESS simulation was taken from mean values published in Casiot et al.²⁴

Determination of Surface Complexation Constants of Tl(I) on Two-Line Ferrihydrite. Two-line ferrihydrite was synthesized in the laboratory as described by Raven et al.³¹ and used for adsorption experiments within 10 days of its synthesis. Adsorption isotherms were obtained for Tl(I) at pH 6.8 ± 0.1 and 7.8 ± 0.1 in 0.01 mol L⁻¹ NaNO₃ solution at initial Tl concentrations of 5, 10, 25, 50, 100, 150, 200, and 300 $\mu\text{g L}^{-1}$ in solution. Three ml of a 16.15 g L⁻¹ ferrihydrite suspension and 400 μL of 1 mol L⁻¹ NaNO₃ solution were added to a 40 mL reaction vessel. The pH of the ferrihydrite suspension, which was agitated with a magnetic

stirrer, was adjusted to the desired pH before each experiment. The desired volume of Tl(I) stock solution was quickly added to the ferrihydrite suspension, and the pH was maintained constant during the reaction between Tl(I) and ferrihydrite by periodic checking and manual adjustment using HCl or NaOH as the titrant. The reaction vessel was kept in the dark by covering it with aluminum paper to avoid photoreduction of Fe(III) and subsequent Tl(I) oxidation during adsorption as observed by Karlsson et al.¹⁶ The suspension was then centrifuged at 2500 g, and the supernatant was passed through a 0.22 μm pore size filter, conditioned with preservative solution, and analyzed immediately for Tl speciation as described above.

Adsorption isotherms were modeled using the CHESS program.²⁹ A two-layer adsorption model³² was used with adsorption of Tl(I) to the ferric oxide surface approximated to $\equiv\text{S}-\text{OH} + \text{Tl}^+ \rightarrow \equiv\text{S}-\text{OTl} + \text{H}^+$. The surface complexation constants were adjusted to obtain the best fit between experimental and modeled data.

Mixing Experiments. Mixing experiments were performed to enable comparison with the processes taking place at the confluence of Reigous Creek and the Amous River. Unfiltered Reigous Creek water from Reigous UC station and Amous River water from Amous UC station were mixed at ratios of 1:0, 1:1, 1:3, 4:21, 1:10, and 0:1 (Reigous Creek water:Amous River water) in acid-cleaned Teflon bottles covered with aluminum paper. The total volume of each mixture was 50 mL. The different mixtures were agitated at ambient temperature on a rotating table at 100 rpm. After 24-h mixing, the solutions were filtered on 0.22 μm pore size filters, acidified with 1% HNO₃, and analyzed for total Tl and Fe concentrations in a similar way as for the field samples. Mn did not precipitate during these experiments, which precluded the oxidation of Tl(I) and subsequent precipitation of Tl₂O_{3(s)} at the surface of Mn oxides as observed by Bidoglio et al.¹⁹

Mixing experiment data were also modeled using the CHESS program. The only phase that was allowed to precipitate was ferrihydrite because it had been clearly identified in Amous River water by X-ray diffraction spectroscopy.³³ Sorption of Zn, Pb, Mn, Co, Ni, Cu, As, Ba, Cd, Sr, Ca, Mg, SO₄, and HCO₃ onto ferrihydrite was taken into account because these constituents are present in the Amous River at concentrations that may exceed that of surface binding sites. For these elements, the surface complexation constants used were from Dzombak and Morel.³² The adsorption of Tl⁺ on hydrous aluminum oxides was not involved in the CHESS simulation because of the lack of available surface

Table 4. Total Trace Element Concentrations (in $\mu\text{g L}^{-1}$) of Amous DC Water during Field Surveys^b

	Fe	As	Zn	Pb	Ba	Mn	Cd	Co	Cu	Ni	Sr	Tl
16/12/04	3545	124.2	646.8	46.3	38.37	393.7	3.873	11.04	9.02	15.68	125.1	1.572
16/12/04 ^a	1986	82.08	463.6	29.32	40.7	389.8	3.049	10.64	11.13	15.06	124.6	1.614
08/02/05	62.15	22.49	88.31	4.752	63.93	37.19	0.58	1.193	1.831	3.908	138.6	0.498
09/03/05	35.98	23.76	46.25	3.014	61.39	6.736	0.225	0.209	1.064	2.055	128.9	0.333
03/05/05	82.79	28.35	109.4	4.055	57.48	66.54	0.806	1.912	1.661	5.141	146.9	0.509
22/06/05	15.93	44.42	22.43	3.126	72.77	6.489	0.104	0.142	1.138	1.836	162.6	0.81
29/07/05	17.86	60.12	19.34	3.633	75.13	4.318	0.081	0.342	0.642	2.128	125.6	0.724
14/10/05	29.8	62.68	67.97	18.9	59.9	18.96	0.408	0.99	1.443	1.868	129.5	0.48
07/11/05	2266	117	356.5	38.24	23.64	114.8	2.259	4.274	11.11	7.014	90.21	0.919
14/12/05	828.4	26.51	350.4	36.34	44.47	137.3	2.304	5.777	6.354	8.35	112.5	0.77
13/01/06	1007	19.75	452.2	52.2	34.54	197.2	3.128	6.657	11.05	9.549	90.4	0.823
14/02/06	3488	42.81	224.7	5.573	32	380.5	1.961	8.126	2.864	6.52	118.7	1.557
16/03/06	221.4	10.76	279.1	18.66	45.73	335.2	2.222	6.855	3.799	4.76	130.9	0.548
16/03/06 ^a	240.9	5.762	212.8	4.381	44.92	333.8	2.028	6.756	2.171	4.584	130.6	0.544
11/04/06	751.3	41.9	265.6	33.79	44.94	147.7	1.743	4.714	6.641	3.138	288.1	0.883
11/04/06 ^a	1380	20.04	103.5	6.477	43.53	144.1	1.105	4.417	2.727	2.615	287.6	0.867
04/05/06	45.99	9.924	94.48	4.017	54.61	71.42	0.892	2.672	1.613	0.228	137.7	0.486
04/05/06 ^a	53.35	8.54	89.77	1.179	54.55	71.02	0.87	2.659	1.383	0.18	137.6	0.481
12/06/06	28	15.46	41.47	2.925	65.34	9.776	0.725	0.364	1.649	4.14	150.9	0.61
12/06/06 ^a	23.55	14.56	38.75	1.53	64.98	9.106	0.712	0.354	1.515	4.079	150.8	0.608
28/07/06	8.85	21.72	43.74	2.487	80	9.597	0.748	0.33	1.612	4.083	190.3	1.027
28/07/06 ^a	73.19	21.85	43.91	2.627	80.01	9.624	0.749	0.332	1.625	4.084	190.3	1.027
22/08/06	28.42	57.17	49.98	1.917	70.7	10.62	0.69	0.393	1.238	3.837	174.9	0.779
22/08/06 ^a	165.7	58.66	50.49	5.008	71.15	10.65	0.693	0.393	1.252	3.837	174.9	0.781
26/09/06	3228	20.27	210.2	6.868	33.64	112.8	1.795	3.014	6.184	6.151	159.8	0.781
26/10/06	1764	15.72	105.4	2.186	21.83	114.4	1.347	3.381	2.196	5.733	85.78	0.893
26/10/06 ^a	221.7	11	99.52	0.688	79.65	114.1	1.257	3.346	1.682	5.672	86.27	0.905
23/01/07	996.5	77.35	241.9	9.695	22.02	295.4	1.997	6.96	3.15	10.35	85.5	1.905
26/02/07	2252	36.54	192.8	3.593	34.69	317	1.812	6.966	1.797	10.84	130.5	1.481
20/03/07	205.2	8.9	232.9	2.02	52.13	249.6	1.683	5.577	1.122	9.191	148.8	0.667
20/03/07 ^a	211.2	9.056	226	2.123	51.82	249.5	1.681	5.571	1.096	9.18	148.8	0.666
12/04/07	291.1	11.32	100.7	1.523	57.19	109.7	0.832	2.734	0.967	6.237	150.1	0.543
12/04/07 ^a	116.3	10.2	107	1.253	57.41	109.8	0.831	2.746	0.98	6.249	150.1	0.539
21/05/07	1335	14.62	144.7	2.217	36.3	217.9	1.488	5.236	1.508	8.625	128.3	1.362
19/06/07	1385	76.5	139.8	7.655	34.52	235.9	1.537	5.577	1.971	8.95	118.8	1.675
19/06/07 ^a	1542	76.92	143	8.678	31.73	235.9	1.548	5.583	2.008	8.95	118.8	1.678
24/07/07	50.29	29.7	29.5	7.72	63.19	25.89	0.268	0.643	0.723	3.692	148.1	0.578
05/09/07	18.46	41.42	22.23	2.91	65.34	72.2	0.26	0.406	12.21	6.614	157.5	3.88
05/09/07 ^a	17.13	54.88	26.41	2.371	65.12	114.9	0.222	0.705	16.91	8.308	157.6	2.306
09/10/07	22.66	31.31	24.04	2.576	64.29	3.811	0.12	0.219	0.454	1.968	149.4	0.53

^a Replicate sample. ^b The pH value and major element concentrations used in CHES simulation were mean values from 17 surveys carried out between 2002 and 2005 (ref 24): pH 7.9; $\text{HCO}_3^- = 261 \text{ mg L}^{-1}$; $\text{SO}_4^{2-} = 76 \text{ mg L}^{-1}$; $\text{Cl}^- = 6 \text{ mg L}^{-1}$; $\text{Mg}^{2+} = 25 \text{ mg L}^{-1}$; $\text{Na}^+ = 4 \text{ mg L}^{-1}$; $\text{Ca}^{2+} = 98 \text{ mg L}^{-1}$; $\text{K}^+ = 1 \text{ mg L}^{-1}$.

complexation constants in the literature and the limited amount of Al in comparison with Fe (ratio 1:6) in water from Reigous Creek. Surface complexation constants used for Tl(I) were those determined in sorption experiments. Composition of Reigous Creek water used in the CHES simulation was as follows: pH = 3.29, $[\text{SO}_4^{2-}] = 549.7 \text{ mg L}^{-1}$, $[\text{Cl}^-] = 14.97 \text{ mg L}^{-1}$, $[\text{Mg}^{2+}] = 38.41 \text{ mg L}^{-1}$, $[\text{Na}^+] = 5.14 \text{ mg L}^{-1}$, $[\text{Ca}^{2+}] = 149.7 \text{ mg L}^{-1}$, $[\text{Fe}^{3+}] = 35103 \mu\text{g L}^{-1}$, $[\text{Al}^{3+}] = 5684 \mu\text{g L}^{-1}$, $[\text{Tl}^+] = 20.92 \mu\text{g L}^{-1}$, $[\text{H}_2\text{AsO}_4^-] = 1915 \mu\text{g L}^{-1}$, $[\text{Zn}^{2+}] = 3498 \mu\text{g L}^{-1}$, $[\text{Pb}^{2+}] = 380 \mu\text{g L}^{-1}$, $[\text{Ba}^{2+}] = 24 \mu\text{g L}^{-1}$, $[\text{Mn}^{2+}] = 1469 \mu\text{g L}^{-1}$, $[\text{Cd}^{2+}] = 31 \mu\text{g L}^{-1}$, $[\text{Co}^{2+}] = 45 \mu\text{g L}^{-1}$, $[\text{Cu}^{2+}] = 183 \mu\text{g L}^{-1}$, $[\text{Ni}^{2+}] = 95 \mu\text{g L}^{-1}$. Composition of Amous River water used in the CHES

simulation was as follows: pH = 8.00, $[\text{HCO}_3^-] = 261 \text{ mg L}^{-1}$, $[\text{SO}_4^{2-}] = 10.58 \text{ mg L}^{-1}$, $[\text{Cl}^-] = 4.65 \text{ mg L}^{-1}$, $[\text{Mg}^{2+}] = 32.15 \text{ mg L}^{-1}$, $[\text{Na}^+] = 3.84 \text{ mg L}^{-1}$, $[\text{Ca}^{2+}] = 120.45 \text{ mg L}^{-1}$, $[\text{Fe}^{3+}] < \text{DL}$, $[\text{Al}^{3+}] < \text{DL}$, $[\text{Tl}^+] = 0.05 \mu\text{g L}^{-1}$, other trace metal concentrations were below detection limits.

RESULTS AND DISCUSSION

Dissolved Thallium. At the source of Reigous Creek (S1), Tl concentrations ranged between 26 and $534 \mu\text{g L}^{-1}$ (Table 2). These concentrations are among the highest ever reported for surface waters^{2,12,21} and references therein³⁴. As a comparison, the maximum Tl concentration found by Xiao et al.³⁴ in the

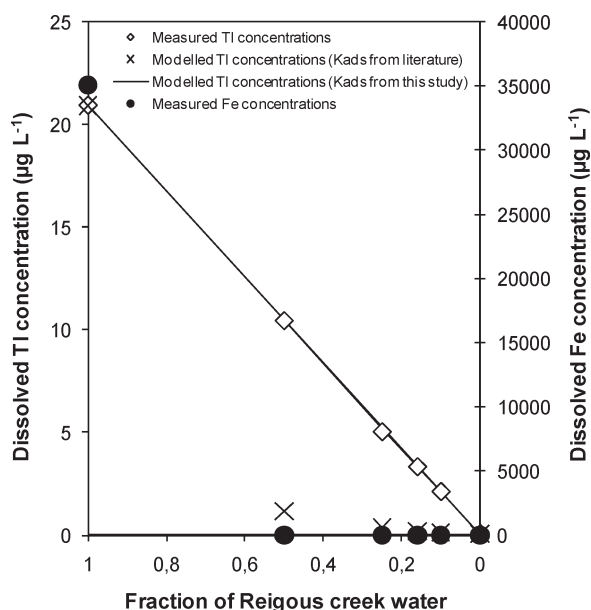


Figure 4. Plot of the dissolved concentrations of Tl and Fe as a function of the fraction of water from Reigous Creek during the mixing of water from Reigous Creek sampled at Reigous UC station and water from the Amous River sampled at Amous UC station in laboratory experiments. Results of model simulation for Tl used either surface complexation constants from the literature ($\log K_{\text{ads}} = 1.31$ for strong sites, 0.24 for weak sites) or those determined in the present study ($\log K_{\text{ads}} = -2.67$ for strong sites, -3.76 for weak sites) and a radius of HFO particles of 2.2 nm, corresponding to a surface area of $438 \text{ m}^2/\text{g}$.

AMD of an Hg–Tl mine in the Guizhou Province, China was $59 \mu\text{g L}^{-1}$. A Tl concentration of $3.24 \mu\text{g L}^{-1}$ was reported in a Zn–Pb mining area in Poland.² Tl concentrations decreased to less than $51 \mu\text{g L}^{-1}$ at Reigous UC station (Figure 1). In the Amous River upstream from the confluence with Reigous Creek (Amous UC), Tl concentrations did not exceed $0.17 \mu\text{g L}^{-1}$. Downstream from the confluence, concentrations increased to values comprised between 1.16 and $5.44 \mu\text{g L}^{-1}$. In the Gardon River immediately downstream from the junction with the Amous River, Tl concentrations were lower than $0.13 \mu\text{g L}^{-1}$, which fitted the range of values measured in the Amous River upstream from the Reigous confluence. Although this value shows recovery of water quality regarding Tl concentrations in the Gardon River, it denotes water contamination when compared to the Tl concentrations of $5\text{--}10 \text{ ng L}^{-1}$ reported by Peter and Viraraghavan⁴ in unpolluted water.

Speciation. Ultrafiltration experiments gave similar Tl concentrations in the fractions below $0.22 \mu\text{m}$ and below 10 kDa at all sampling stations along Reigous Creek and at Amous DC station (Table 3). This indicates that Tl was not associated with the colloidal phase.

Tl(I) predominated over Tl(III) at all sampling stations on Reigous Creek, representing more than 98% of the total concentration of Tl in the dissolved phase (Table 3). Tl(III) was undetectable at the Amous and Gardon River stations. These results are in agreement with the positioning of most field Eh and pH data in the stability domain of Tl^+ in the Eh–pH diagram (Figure 2). They differ from the experimental results of Lin and Nriagu,^{12,35} who reported Tl(III) as the predominant Tl species in lake and river water. Complexes of Tl(I) with natural organic matter might represent 8% of aqueous Tl(I) species in the Amous

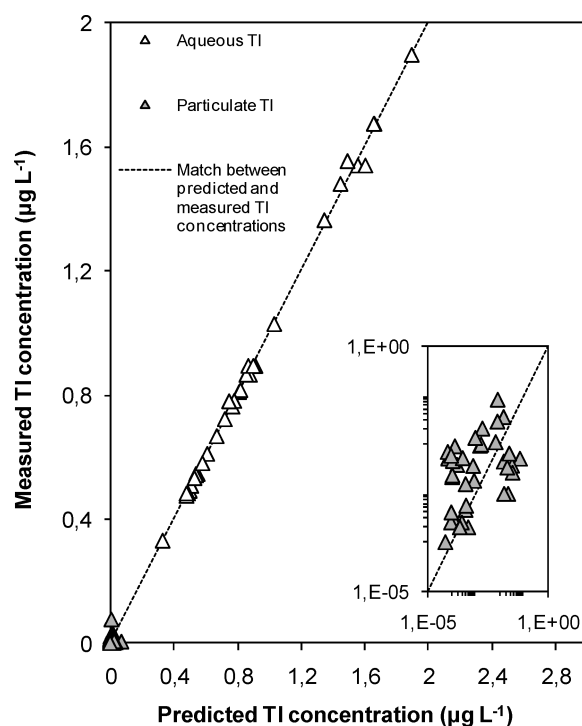


Figure 5. Comparison of concentrations of particulate and aqueous Tl measured in the field and those predicted from total Tl concentrations using CHES. Predictions were made from intrinsic surface complexation constants determined in the present study and a radius of HFO particles of 2.2 nm, corresponding to a surface area of $438 \text{ m}^2/\text{g}$. Sorption of Zn, Pb, Mn, Co, Ni, Cu, As, Ba, Cd, Sr, Ca, Mg, SO_4 and HCO_3 onto ferrihydrite was taken into account with surface complexation constants from Dzombak and Morel.³² Total trace element concentrations used in the simulation are presented in Table 4. Dashed lines indicate a perfect match between predicted and measured concentrations.

River, although it was not demonstrated experimentally. Some of the Eh and pH data from Amous DC station were positioned in the stability domain of dorallcharite ($\text{TlFe}_3(\text{SO}_4)_2(\text{OH})_6$) (Figure 2), indicating that the precipitation of this phase might proceed occasionally in Amous River. The precipitation of other Tl(I)-bearing solids such as Lanmchangite ($\text{TlAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), which was shown to be the solubility controlling phase in acidic solutions enriched with SO_4^{2-} and Al^{3+} such as those in Lanmchange¹⁰ did not appear to be favored in the acid Reigous Creek or in Amous River. The minor amounts of dissolved Tl(III) detected in the Reigous Creek could be in the form of a chlorocomplex TlCl_2^+ .

Total and Particulate Tl. Concentrations of particulate Tl ranged from 2×10^{-4} to $1.8 \mu\text{g L}^{-1}$ and were low compared to dissolved values, generally less than 10% of total Tl (Table 2). The dissolved to particulate distribution coefficient $\log K_d$ increased slightly from Reigous Creek ($\log K_d = 2.5 \text{ L kg}^{-1}$) to downstream sites on the Amous ($\log K_d = 3.1\text{--}3.7 \text{ L kg}^{-1}$) and Gardon ($\log K_d = 4.6 \text{ L kg}^{-1}$) Rivers, indicating increasing association of Tl with particulate matter. Nevertheless, such low $\log K_d$ values revealed little affinity of Tl for mine-derived suspended particulate matter, which was predominantly composed of hydrous ferric oxides in the Amous River.²⁴ The low affinity of Tl^+ for hydrous ferric oxides was reflected by the results of sorption experiments, the best fit between the experimental data and those modeled using CHES being achieved for surface complexation constants of $10^{-2.67}$ for strong sites and $10^{-3.76}$ for weak sites (Figure 3); these

values were 4 log units lower than those derived from linear free energy relationships.²¹

The low affinity of Tl⁺ for Fe oxide phases accounted for the nearly conservative behavior of Tl during the mixing of waters from Reigous Creek and the Amous River. Despite intensive Fe precipitation, Tl concentrations nearly followed the mixing line between the two end-members (Figure 4). This behavior, which contrasted with the high rate of removal of other metals and As,²⁴ was well simulated by the CHESS model provided the stability constants determined in sorption experiments were used rather than values from the literature.²¹ In the same way, this new set of constants reasonably satisfactorily simulated the distribution of aqueous and particulate Tl concentrations observed in the Amous River during our surveys (Figure 5).

AUTHOR INFORMATION

Corresponding Author

*Phone: +33 467143356. Fax: +33 467144774. E-mail: casiot@msem.univ-montp2.fr.

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