



Thallium in the hydrosphere of south west England

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ABSTRACT

Thallium is a highly toxic metal whose environmental concentrations, distributions and behaviour are not well understood. In the present study we measure the concentrations of Tl in filtered and unfiltered samples of rain, tap, river, estuarine and waste waters collected from south west England. Dissolved Tl was lowest ($<20 \text{ ng L}^{-1}$) in tap water, rain water, treated sewage and landfill effluents, estuarine waters, and rivers draining catchments of sandstones and shales. Concentrations up to about 450 ng L^{-1} were observed in rivers whose catchments are partly mineralized and where metal mining was historically important, and the highest concentration ($\sim 1400 \text{ ng L}^{-1}$) was measured in water abstracted directly from an abandoned mine. Compared with other trace metals measured (e.g. As, Cd, Co, Cr, Cu, Ni, Pb, Zn), Tl has a low affinity for suspended particles and undergoes little removal by conventional (hydroxide precipitation) treatment of mine water.

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1. Introduction

Thallium is a relatively rare element that is widely distributed in the environment, presumably because of its volatility, with an average lithospheric concentration of $1 \mu\text{g g}^{-1}$ (Smith and Carson, 1977). A few Tl-bearing minerals exist (e.g. lorandite, TlAsS_2 , and avicennite, Tl_2O_3) but the metal is encountered mainly in minerals of potassium, its biogeochemical analogue in many respects, such as alkali feldspars and micas, in coal, and in many sulphidic minerals. Consequently, Tl is usually recovered for use in the electrical, semiconductor and chemical industries as a byproduct metal from flue dusts and residues arising from the smelting and refining of Cu, Zn and Pb ores. As a contaminant, Tl enters the environment largely from the burning of coal and from metal smelting.

Thallium is also highly toxic; it is an Environmental Protection Agency (EPA) priority pollutant and has been classified as a “dangerous substance” by the EU (Directive 67/548/EEC). It has been reported to be more acutely toxic than Hg, Cd and Pb in mammals (Peter and Viraraghavan, 2005) and is of comparable toxicity to Pb to the aquatic amphipod, *Hyalella azteca* (Borgmann et al., 1998). Despite its toxicity, however, very little information exists on the environmental behaviour of Tl and, in particular, its mobilisation, distribution, impacts and fate in aquatic systems. This may, partly, be attributed to the relatively low economic value of the metal and, until recently, difficulty associated with its analysis

in natural samples. What is currently understood about Tl in the hydrosphere may be summarized as follows. A global average Tl concentration in river water, based on the analysis of samples from 12 large rivers, is 6.6 ng L^{-1} (Nielsen et al., 2005), and a mean sea water concentration has been estimated to be about 1.3 ng L^{-1} (Rehkämper and Nielsen, 2004). Under conditions typical of most surface waters Tl(I) is predicted to be the dominant species, although empirical evidence exists for the occurrence of Tl(III) in some environments (Lin and Nriagu, 1999). Interactions between Tl(I) and organic ligands are weak and equilibrium calculations indicate that the free ion is the principal species in most natural waters, including in sea water where chloride complexes are predicted to comprise only about 35% of total Tl(I) (Kaplan and Mattigod, 1998). Interactions with sediment appear to take place by adsorption to Mn oxides and through irreversible cation fixation onto micaceous minerals (Kaplan and Mattigod, 1998; Rehkämper and Nielsen, 2004) but particle-water distribution coefficients defining such interactions are amongst the lowest reported for trace metals in natural waters (Turner et al., 2010). Thallium is accumulated by algae and plankton (Flegal et al., 1986; Twiss et al., 2003) but, as with sediment, the extent of these interactions is low compared with those defining other trace metals.

In the present study, we determine Tl concentrations in water samples collected from the hydrosphere of south west England. Analysis is accomplished directly by the latest generation of quadrupole inductively coupled plasma-mass spectrometers. Specifically, we measure concentrations in both filtered and unfiltered aliquots of samples of river water, rain water, tap water, estuarine water, treated sewage effluent, treated landfill leachate

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and treated and untreated mine-adit waters. To our knowledge, Tl concentrations for this area have only ever been reported for a number of stream waters, sediments and topsoils collected from the River Tamar catchment by the British Geological Survey (Rawlins et al., 2003). Our results will enable the relative significance of different natural and anthropogenic sources of Tl to south west England and, potentially, the hydrosphere more generally, to be evaluated. We also measure its fractionation in these samples between the aqueous and particulate compartments and concurrently determine a range of other geochemically important and anthropogenically-impacted metals in order to improve our understanding of the geochemical behaviour of Tl in the hydrosphere.

2. Materials and methods

2.1. Sample sites

Samples were collected from two regions of south west England at the locations shown in Fig. 1 and as listed in Table 1 between October and December of 2010 (unless otherwise indicated in the Table). Twenty-eight samples of river water were collected from a number of catchments. Samples coded R1–R3 were collected from a small river system whose geology is dominated by Devonian slates and sandstone. Remaining river water samples (R4–R27) were collected from systems draining catchments containing, additionally, Carboniferous granite and, therein, variable degrees of epithermal and hypothermal mineralisation. Within these catchments, extensive mining for a number of metals (but principally Sn and Cu) has been important. Although mining activities began to decline from the middle of the 19th century and have since ceased completely, waste waters from old adits, shafts and spoil heaps remain sources of metal pollution to the regional hydrosphere

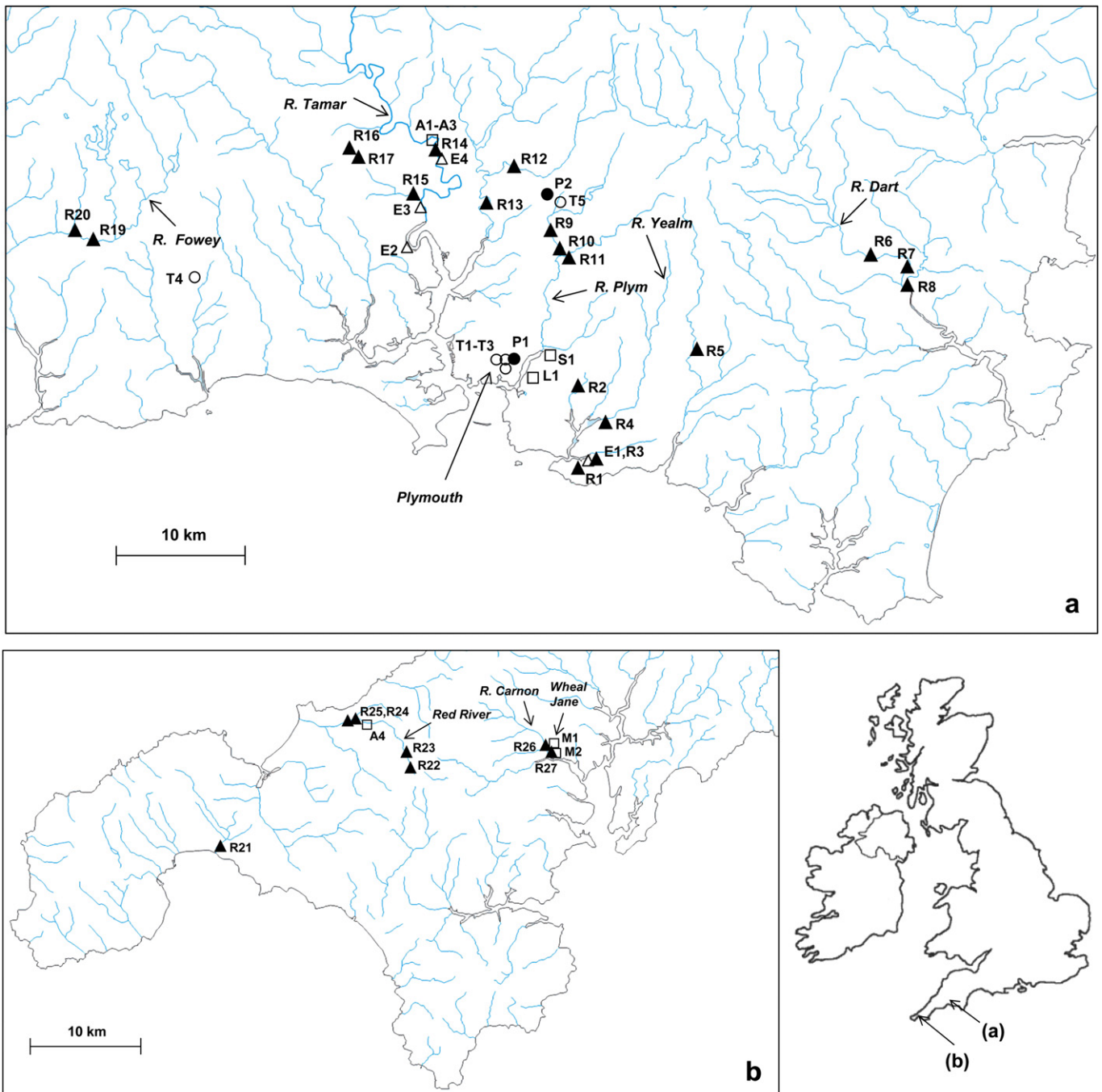


Fig. 1. Locations of the samples collected for Tl analysis and as defined in Table 1 (○, tap water; ●, precipitation; ▲, river water; △, estuarine water; □, waste water).

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