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Selenium in sediments and biota from estuaries of southwest England

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ABSTRACT

Selenium concentrations have been measured in sediment, fucoid macroalgae and macroinvertebrates from four estuaries of SW England (Yealm, Plym, Looe, Fal). Sediment concentrations ranged from about 0.4 μg g^{-1} in the Yealm to 1.49 μg g^{-1} at one site in the Plym. Concentrations in *Fucus vesiculosus* (0.05–0.31 μg g^{-1}) and *F. ceranoides* (0.05–0.51 μg g^{-1}) were significantly lower than corresponding concentrations in sediment but there was no correlation between algal and sediment concentrations. Selenium concentrations in *Littorina littorea* (∼4 μg g^{-1}), *Hediste diversicolor* (2.82–12.68 μg g^{-1}), *Arenicola marina* (∼17 μg g^{-1}) and *Scrobicularia plana* (1.18–6.85 μg g^{-1}) were considerably higher than concentrations in macroalga or sediment, suggesting that Se is effectively accumulated from the diet. Although Se concentrations in some invertebrates exceed toxicity thresholds for the diet of predacious birds and fish, no specific evidence for Se toxicity exists in these estuaries.

Selenium occurs with a crustal abundance between 0.05 and 0.09 μg g^{-1} (Ayres and Hellier, 1998). Significantly higher concentrations are encountered in some phosphatic rocks and, because of its chemical similarity to sulphur, in sulphidic deposits. Selenium is generally recovered as a by-product in the treatment of copper sulphide ores for use in the electronics and glass industries, in pigments, fungicides, rubbers and paints, and as a dehydrogenation catalyst. Important anthropogenic sources of Se include phosphate mining, nonferrous metal smelting, coal combustion, agricultural drainage and fly ash disposal.

In the aquatic environment, Se exists in four valence states: namely, as elemental selenium, Se(0), as Se(II) in organic selenides, as Se(IV) in the oxyanion selenite (SeO_3^{2-}) and as Se(VI) in the oxyanion selenate (SeO_4^{2-}). All forms can be incorporated into particulate matter through adsorption and copreciptation but elemental Se is often the dominant species in estuarine and freshwater sediments (Schlekat et al., 2000), being precipitated by both bacterial dissimilatory reduction and abiotic geochemical processes. Organic selenide, mainly as seleno-amino acids in peptides and proteins, is produced by plants after uptake of selenite or selenate and is the principal form of Se in biogenic particulate matter (Doblin et al., 2006).

Unlike phytoplankton and other primary producers, the uptake of Se by invertebrate consumers is largely through ingestion (Zhang et al., 1990; Peters et al., 1999; Linville et al., 2002). Critical to Se uptake from particulate matter, therefore, are the nature of particles and the chemical form of particulate Se; for example, Se is more bioavailable in bacteria than in sediment and in organic form than in elemental form (Doblin et al., 2006). Selenium accumulated by these consumers is then efficiently transferred to their predators (fish, birds, mammals) with biomagnification resulting in many cases (Stewart et al., 2004). A major concern in this respect is that while Se is a nutritionally essential metalloid to many animals and plants, it is also toxic at high concentrations. Moreover, the window between essentiality and toxicity is often narrow, with suggestions that a diet containing >1 μg g^{-1} but <5 μg g^{-1} is required for normal growth and development (Bryan and Langston, 1992). At higher concentrations, Se causes deformities in embryos or inhibits egg hatchability because of its propensity to substitute for sulphur in the tertiary structures of proteins (Linville et al., 2002). Thus, well documented are the adverse reproductive effects and mortality in fish and wildfowl populations inhabiting environments contaminated by Se (Gillespie and Baumann, 1986; Ohlendorf et al., 1986; Hamilton, 1999).

Estuaries are highly productive habitats hosting a diversity and abundance of detritus feeders that are the main food source for many fish and wading birds. Given the toxicity of Se, and its accumulation by aquatic invertebrates and propensity for trophic transfer, it is perhaps surprising that this metalloid has received relatively little attention in estuaries, aside from in those environments known to receive (or have received) specific anthropogenic Se inputs (Schlekat et al., 2000; Kirby et al., 2001). Accordingly, the present study reports concentrations of Se in sediment and in biomonitors of metal and metalloid contamination (fucoid macroalgae, deposit-feeding invertebrates and a grazing gastropod) from four macrotidal estuaries of south west England. No specific evidence exists for Se enrichment or toxicity in these estuaries. Rather, the study aims to provide quantitative information on the accumulation of Se by different indicator organisms commonly

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encountered on the estuarine shores of northern Europe and the Atlantic coast of North America and, therefore, dietary concentrations of the metalloid typically available to predatory fish and wildfowl.

Sampling was undertaken as part of two independent research projects and on different occasions during 2012 in the estuaries of the Yealm, Plym, Looe and Fal at the locations shown and coded in Fig. 1. The catchments of the estuaries are currently dominated by agricultural land, forest and open moorland. However, because of epithermal and hypothermal mineralisation within their watersheds, mining for a number of metals and metalloids (e.g. Sn, Cu, Zn, Ag, Pb, As) was historically important. Although mining began to decline from the middle of the 19th century and has since ceased completely, waste waters from old adits, shafts and spoil heaps remain significant riverine sources of metal contamination to many western tributaries of the Fal and, for Cu, Ag and Pb, to the West Looe River (Rainbow et al., 2011). Other, contemporary sources of metals and metalloids to these estuaries are associated with shipping, boat maintenance and consented discharges (urban sewage and, in the lower Plym, landfill leachate).

The biota selected for study were two species of Phaeophyta (the fucoid macroalgae, *Fucus vesiculosus* and *Fucus ceranoides*), three deposit-feeding invertebrates (the polychaete worms, *Hediste diversicolor* and *Arenicola marina*, and the filter-feeding/deposit-feeding bivalve mollusc, *Scrobicularia plana*) and a grazing snail, *Littorina littorea*. These organisms have a wide salinity tolerance and have been commonly employed as biomonitors of metal and metalloid contamination in estuaries, and in particular in the

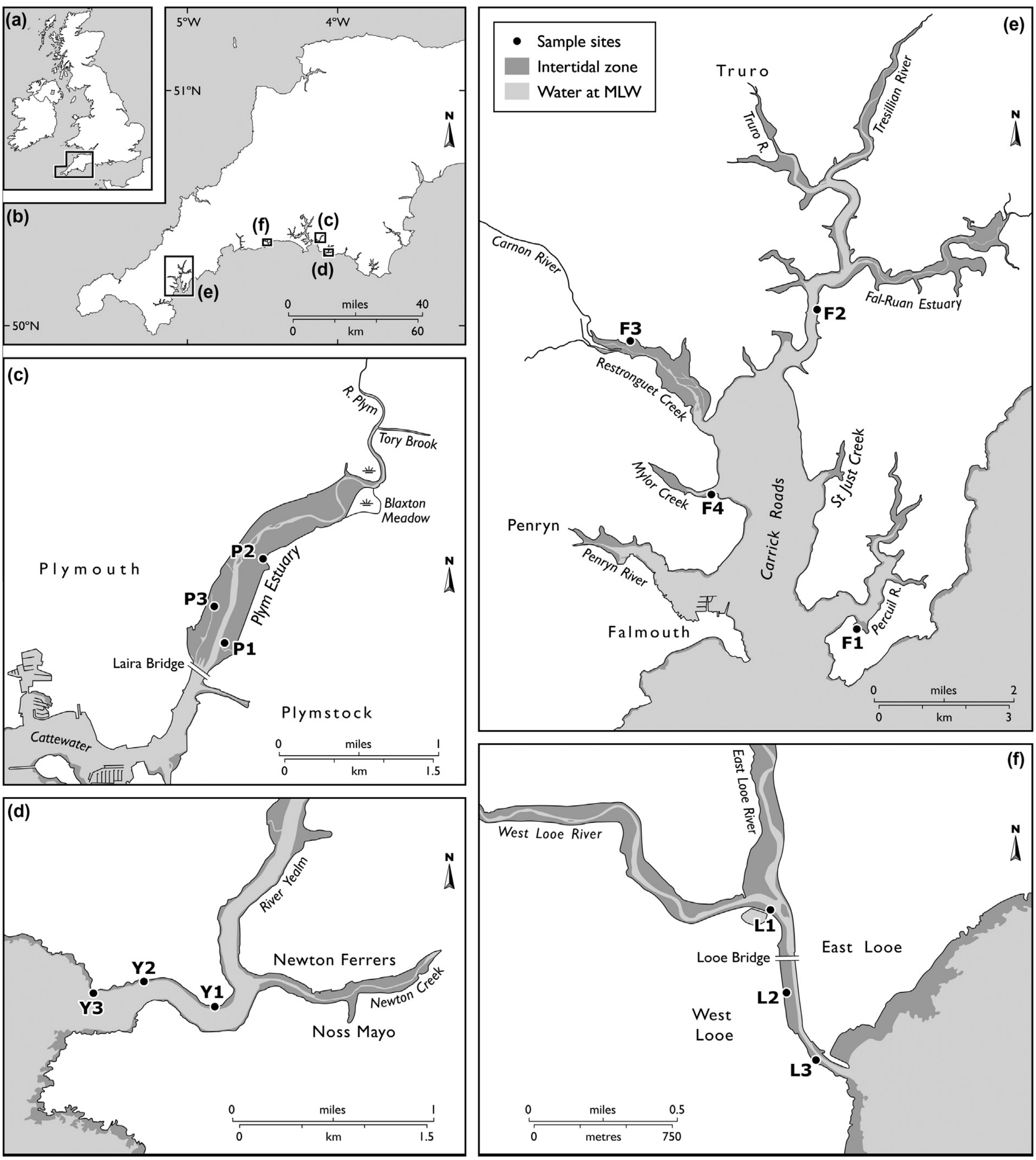

Fig. 1. South west England (a), the locations of the four estuaries (b), and sampling locations in the Plym (c), Yealm (d), Fal (e) and Looe (f).