



On site determination of trace metals in estuarine sediments by field-portable-XRF

Andrew Turner*, Alex Taylor

School of Geography, Earth and Environmental Sciences, Plymouth University, Drake Circus, Plymouth PL4 8AA, UK



ARTICLE INFO

Keywords:

Portable-XRF
Estuarine sediments
Trace metals
Contaminants
On site

ABSTRACT

A portable x-ray fluorescence (XRF) spectrometer and mobile test stand have been employed to examine the feasibility of on site measurements of trace metals in estuarine sediment. In the laboratory, the instrument was able to detect the trace metals: As, Cr, Cu, Pb, Sn and Zn; and the geochemical proxy metals: Ca, Fe, K and Rb; in both fresh and freeze-dried surficial samples from the Tamar and Tavy estuaries, southwest England, that had been emplaced in polyethylene bags over the detector window. The presence of interstitial water in fresh samples acted as both a diluent of sediment mass and an attenuator of incident and fluorescent x-rays, resulting in measured (fresh weight) metal concentrations that were significantly lower than corresponding (dry weight) concentrations derived from dry analyses. Gravimetric correction for fractional water content ($f_w \sim 0.2\text{--}0.6$) gave rise to results that were within 20% of those derived from dry analyses with the exception of K, whose relatively low energy fluorescent x-rays were subject to significant attenuation from the aqueous medium; further x-ray attenuation was observed for both K and Ca through the sample bag, thereby limiting the usefulness of the approach for these metals. A relationship between the concentration of Rb and f_w in fresh samples suggests that Rb may be used as a proxy for interstitial water content through its covariance with sediment grain size. Accordingly, on site measurements of trace metals of sufficient fluorescent x-ray energies may be corrected empirically with respect to Rb in order to simultaneously account for variations in granulometry and mass contribution of water. On this basis, results from an axial transect of the Tamar and an intertidal transect in the Tavy were able to detect variations in trace metal concentrations that were consistent with known sources and geochemical behaviours.

1. Introduction

Estuaries represent the river-ocean interface of the hydrosphere and play a key role in the transportation, modification and storage of materials and chemicals derived from natural erosion and anthropogenic inputs in the watershed [24]. Estuarine sediments are particularly significant vectors and reactors in this respect since they undergo considerable internal recycling through resuspension-deposition and provide a high surface area for the adsorption-desorption of a variety of chemicals [31]. Trace metal(loid) contaminants, such as As, Cu, Pb and Zn, interact strongly with suspended and deposited estuarine sediment through a variety of processes, and concentrations in intertidal or subtidal deposits often provide an indication of the anthropogenic signature in the catchment [12]. Accordingly, measurements of trace metals in sediments form an integral component of many assessments of estuarine quality or status [18,3,5].

Conventionally, metals and metalloids (hereafter referred to as

metals) in estuarine and coastal sediments are determined by a suitable spectrophotometric technique following total or quasi-total digestion of dried samples by flux fusion or combined acid attack [33,34]. Analysis by inductively coupled plasma spectrometry or atomic absorption spectrometry, for example, is rapid and relatively straightforward, but digestion may be time- and resource-intensive and can generate considerable quantities of hazardous waste. Alternative, non-destructive approaches for measuring metals in sediments include neutron activation analysis and benchtop x-ray fluorescence (XRF) spectrometry [1,2] but equipment may be expensive to run and, regarding the former, access to a nuclear reactor is required. Moreover, both sample preparation, involving milling and pelletisation or packing, and sample analyses are time-consuming.

With the miniaturisation of x-ray tubes, improvements in detector resolution and advancements in signal processing capability, portable, energy-dispersive XRF has gained increasing use for the rapid, cost-effective and non-destructive analysis of metals in particulate geosolids

* Corresponding author.

E-mail address: aturner@plymouth.ac.uk (A. Turner).

<https://doi.org/10.1016/j.talanta.2018.08.024>

Received 7 May 2018; Received in revised form 1 August 2018; Accepted 6 August 2018

Available online 10 August 2018

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over the past two decades [21,22]. Minimal sample processing (sieving and drying) has allowed a high throughput of samples in the laboratory, but measurements may also be performed in the field if material is sufficiently fine, homogeneous and dry [10]. In this respect, estuarine sediments are more challenging because of a relatively high content of interstitial water. Thus, besides the risk of damaging sensitive components within the detector window, water acts as a diluent of sediment mass and an attenuator of incident (primary) and fluorescent (secondary) x-ray, effects that reduce signal intensity and tend to underestimate true (absolute) concentrations.

Attempts have been made to measure metals in sediment samples in the fresh or part-dried state by portable XRF, in both the laboratory and in the field, with results deemed to be of sufficient quality to screen for heavy metal contamination or to aid decision-making for management purposes [13,14,16,26,8]. However, the significance of water and suitable means for its correction are rarely addressed in a systematic or quantitative manner that allow absolute, dry weight concentrations to be accurately predicted. To this end, we evaluate the potential of a battery-powered Niton XRF instrument coupled with a mobile test stand for the field measurement of trace metals in estuarine sediments. Specifically, the effects of x-ray attenuation by suitable containers and by interstitial water are examined in controlled experiments in the laboratory, with results compared with those obtained from an optimised geometry whereby samples had been freeze-dried and milled prior to packing into customised XRF sample cups. A configuration of the instrument and stand is tested in the field, with means of correcting on site results for water content explored which are based on gravimetric measures or the use of analyte proxies for moisture.

2. Materials and methods

2.1. XRF instrumentation and configuration

In the current study, samples were analysed for various metals either in the laboratory or in the field using a Niton XL3t 950 He GOLDD + portable XRF spectrometer. Measurements were conducted in a ‘mining’ mode and with a beam width of 8 mm (equivalent to a measurement area of 50 mm²) for a total time of 60 s, comprising successive counting periods of 30 s at 50 kV/40 μA (main filter), 15 s at 20 kV/100 μA (low filter) and 15 s at 50 kV/40 μA (high filter). This mode is capable of detecting more than 20 elements in particulate geosolids (from K to Bi) but here we focus on trace metals that were readily detected in a preliminary study of estuarine sediments (As, Cr, Cu, Pb, Sb, Sn, Zn; [32]) as well as metals that act as potential geochemical proxies or indicators of analytical performance (Ca, Fe, K, Rb).

In the laboratory, the instrument was configured nose-upwards in a 4000 cm³ accessory stand and activated remotely through a laptop and at an operator distance of 2 m. In the field, the instrument was configured nose-upwards in a 300 cm³ portable test stand (described in detail elsewhere; [29]) and activated and operated likewise. Spectra arising from sample counting were quantified by fundamental parameter coefficients to yield metal concentrations in μg g⁻¹ and with a measurement counting error of 2σ (95% confidence) that were downloaded to the laptop via Niton data transfer (NDT) software.

2.2. Sampling and sample characteristics

Estuarine sediment samples were collected from the Tamar and its tidal tributary, the Tavy. The watershed of the Tavy and the upper catchment of the Tamar are dominated by moorland, managed forest and agricultural land but remain highly contaminated by various trace metals (and mainly As and Cu) from historical mining activities, while the lower catchment of the Tamar is partly urbanised and supports various facilities for the maintenance and repair of boats and ships. Fine, surficial (depth < 5 mm) intertidal muds and silts were targeted at the locations shown in Fig. 1 and during 2017 and early 2018 in order

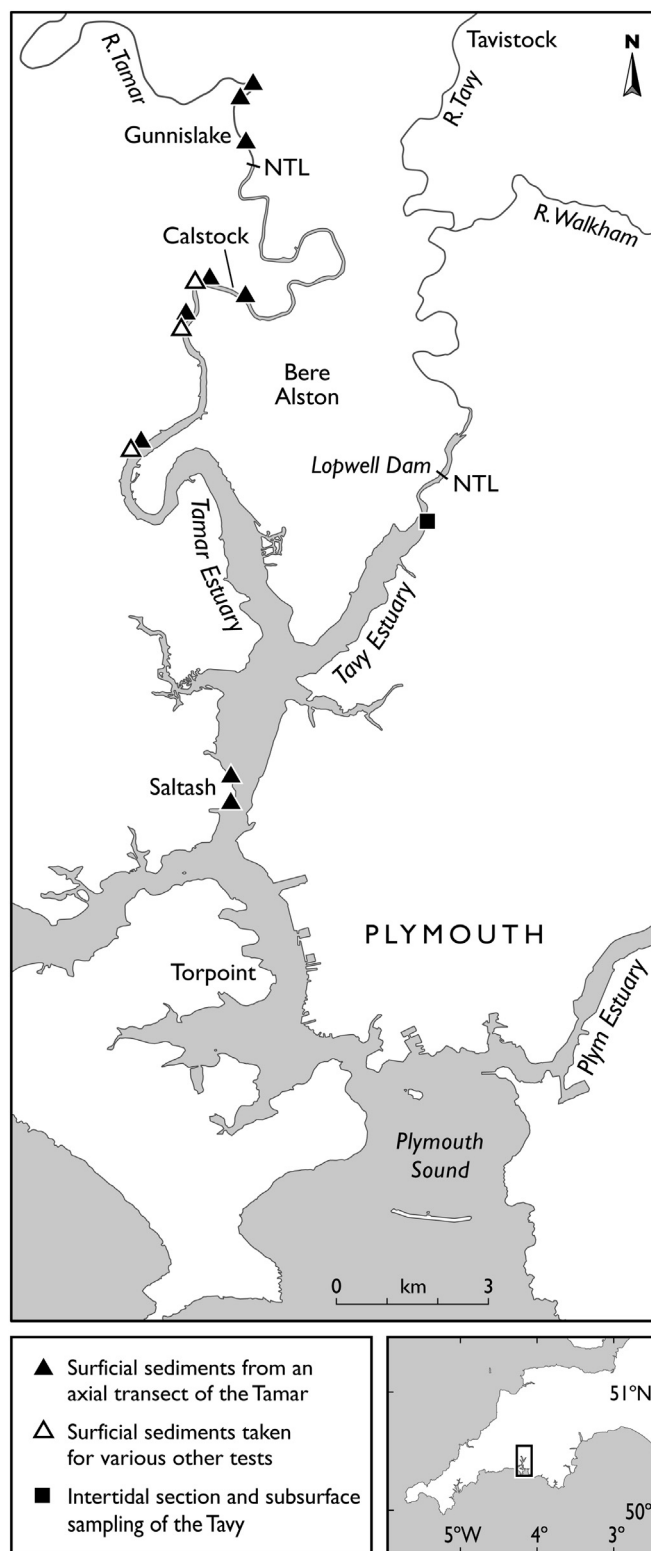


Fig. 1. Sampling locations in the Tamar and Tavy estuaries, southwest England. NTL = normal tidal limit.

obtain a variety of relatively homogeneous materials that required minimal processing. Specifically, (i) a number of samples were collected from the Tamar and Tavy as and when required in order to undertake various tests in the laboratory, (ii) a field transect was undertaken along the axis of the Tamar at nine sites from above its tidal limit to about 7 km from the mouth (including locations known to be

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