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Novel use of field-portable-XRF for the direct analysis of trace elements in marine macroalgae☆

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ABSTRACT

Samples of dried marine macroalgae (*Fucus serratus*, *Palmaria palmata* and *Ulva lactuca*) have been analysed for trace elements by a novel, non-destructive approach involving a Niton field-portable-X-ray fluorescence (FP-XRF) spectrometer configured in a low density plastics mode with thickness correction. Detection limits for a 200-s counting time ranged from <5 μg g^{-1} for As and Pb in *F. serratus* and As in *P. palmata* to several tens of μg g^{-1} for Cd, Sb and Sn in all species tested. Arsenic, Cu, Pb and Zn were detected by the XRF in samples collected from a protected beach ($n = 18$) and in samples therefrom that had been exposed to additional aqueous elements in combination ($n = 72$) with concentrations returned (in μg g^{-1}) ranging from 3.9 to 39.7 for As, 13.0 to 307 for Cu, 6.1 to 14.7 for Pb and 12.5 to 522 for Zn. Independent measurements of trace elements in the macroalgae by ICP-MS following nitric acid digestion revealed a direct and significant proportionality with concentrations returned by the XRF, with slopes of the XRF-ICP relationships (As = 1.0; Cu = 2.3; Pb = 2.4; Zn = 1.7) that can be used to calibrate the instrument for direct measurements. The approach shows potential for the in situ monitoring of macroalgae in coastal regions that is currently being investigated.

1. Introduction

With the miniaturisation of X-ray sources, reduction in battery power requirements, and improvements in detector resolution, detection limits and fundamental parameter calibrations, field-portable-X-ray fluorescence (FP-XRF) spectrometry has gained increasing use for the rapid, cost-effective and non-destructive analysis of trace elements in environmental solids over the past two decades (Bosco, 2013). Most publications have described the analysis of dried and sieved or pulverised soils, tailings, dusts and sediments (Radu and Diamond, 2009; Parsons et al., 2013; McComb et al., 2014), with many studies extending the application for screening in situ (Higueras et al., 2012; Weindorf et al., 2012). Recently, means of measuring trace elements by FP-XRF in low density environmental particulates, like paints and plastics, have also been described and tested (Nakashima et al., 2012; Turner et al., 2014; Ytreberg et al., 2015). Because polymers are composed of light elements that are weak absorbers of X-rays, the intensity of characteristic fluorescent X-rays is dependent, in part, on sample thickness (Piorek, 2004). To compensate for low density samples that are thinner than a few mm, therefore, application of a thickness correction algorithm based on measured sample thickness is an important, additional consideration in the fundamental parameter XRF computations (Turner and Solman, 2016).

In the present study, we hypothesize that the XRF approach developed for use on plastics and paints could be applied to the determination of trace elements in marine macroalgae, whose compositional and thickness characteristics bear similarities to those of synthetic polymeric films. Many species of marine macroalgae accumulate trace metals and metalloids from sea water to concentrations several orders of magnitude greater than their environment and serve as potentially useful sentinel organisms of local environmental contamination (Varma et al., 2011; Reis et al., 2014; Malea et al., 2015). While conventional analysis of macroalgae entails digestion of dried material in concentrated mineral acid and subsequent analysis by, for example, anodic stripping voltammetry, atomic absorption spectrometry or inductively coupled plasma (ICP) spectrometry, the throughput of multiple samples can be time-consuming and labour-intensive. Here, therefore, we investigate the feasibility of a FP-XRF spectrometer (Niton XL3t) calibrated for plastics and with thickness correction

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capability for the analysis of a variety of trace metals and metalloids in dried samples of a brown (*Fucus serratus*), red (*Palmaria palmata*) and green (*Ulva lactuca*) seaweed. As an independent and comparative measure of the elemental content of the algae, we analyse subsequently digested samples by ICP-mass spectrometry. Although the XRF study is conducted in a bench-top accessory stand, we also discuss the potential for the approach to be employed for in situ monitoring and screening of coastal and estuarine macroalgae.

2. Materials and methods

2.1. Sampling and sample preparation

Individuals of *Fucus serratus*, *Palmaria palmata* and *Ulva lactuca* were collected at low tide during November 2015 from the intertidal rock pools at Wembury, a protected beach in south Devon, SW England (50°19′03.8″N, 4°05′04.5″W). Samples were transported to the Plymouth University laboratory in zip-locked polyethylene bags where they were washed in a 1:9 solution of ethanol:sea water before surfaces were gently scraped with a polyethylene spatula to remove particulate matter and epiphytes (Gledhill et al., 1998). Different species were then grouped and transferred to ten-litre polyethylene aquaria containing aerated, coastal sea water (salinity ~ 32; pH ~ 8.0) that had been collected in bulk from Plymouth Sound and filtered through 0.6 μm extruded carbon. Samples were acclimated for three to six days under an irradiance of 125 μmol m^{-2} s^{-1} on a 16:8 h light:dark cycle at 14 ± 2 °C.

In a first experiment, three samples of each species were removed from the aquaria and cut into two halves longitudinally. To compare drying method on XRF analysis (through potential differences in sample integrity, flatness, smoothness and thickness), one half of each sample was oven-dried at 80 °C for 24 h while the other half was frozen and freeze-dried for 48 h using an Edwards Super Modulyo. These samples are hereafter referred to as 'baseline' and contain ambient concentrations of metals and metalloids.

In a second experiment, 36 one-litre clear polyethylene tanks were filled with filtered sea water. To 27 tanks, one of three concentrations of a combined solution of As, Cu and Zn was added (the rationale for using these elements was based on results from the 'baseline' experiment and as discussed below). Specifically, a stock solution containing $Na_2HAsO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ and $ZnSO_4 \cdot 7H_2O$ (ReagentPlus®, Sigma-Aldrich) was used to obtain respective concentrations of As, Cu and Zn of 5, 50 and 500 μg L^{-1}, 7.5, 75 and 750 μg L^{-1} and 10, 100 and 1000 μg L^{-1}. Twelve individuals of each species were then allocated to aquaria, with three replicates per treatment that included controls without element addition. After seven days' exposure under the acclimation conditions described above, individuals were removed and cut in half longitudinally, with one half being oven-dried and the other half freeze-dried. These samples, hereafter referred to as 'exposed', were designed to contain a range of elevated concentrations of As, Cu and Zn representative of more contaminated coastal environments.

2.2. FP-XRF analysis

In order to minimise confounding effects arising from differential accumulation of elements by different parts of the macroalgae, sections from the mid-thallus were dissected from each dried sample. Sections were analysed for trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn and Zn) by energy dispersive FP-XRF using a battery-powered, field portable (1.3 kg) Niton XRF analyser (model XL3t 950 He GOLDD+). The instrument employs an X-ray tube with a silver anode operating at up to 50 kV and 200 μA as the source of sample excitation, and is fitted with a geometrically optimised large area silicon drift detector to detect and register characteristic fluorescent X-rays from the sample.

Elemental concentrations in macroalgal sections were determined using a low density plastics mode by way of a fundamental parameters-based alpha coefficient correction model. Because the intensity of fluorescent X-rays arising from low density materials is affected by the depth of the sample, a thickness correction algorithm, employing a compensation for mass absorption coefficient based on Compton scatter and calibrated down to 0.05 mm, was also applied after sample thickness had been measured with digital callipers.

The XRF was used in the laboratory in a bench-top accessory stand (with the nose pointing upwards) and was connected to a Fujitsu laptop computer via USB and a remote trigger. Samples were placed on to a SpectraCertified Mylar polyester 3.6 μm film which was then positioned such that the smoothest and flattest part of the sample lay directly and centrally above the 8 mm XRF measurement window, a process aided by referring to real-time video footage generated by an integrated CCD camera adjacent to the detector. To increase the effective depth of the thinnest samples (mainly *Ulva*), sections were folded or cut and stacked before being placed above the window. On closing the steel shield of the stand, measurements with appropriate thickness correction were activated through the laptop for a total period of 200 s; specifically, counting was performed for 100 s each in a low energy range (20 kV and 100 μA) and main energy range (50 kV and 40 μA). Decreasing counting time was found to reduce the number of cases in which elements were detected while increasing counting time (up to 600 s) did not significantly increase detectable cases but resulted in a reduction in counting error.

2.3. Macroalgae digestion and analysis by ICP

As an independent and more sensitive measure of the elemental composition of the macroalgae, all baseline ($n = 18$) and exposed ($n = 72$) sample sections were subsequently acid-digested and analysed by inductively coupled plasma-mass spectrometry (ICP-MS). Thus, samples of about 0.1 g were accurately weighed into individual Teflon tubes to which 2 ml aliquots of HNO_3 (Fisher Chemical TraceMetal™ Grade) were added. The contents were digested in a CCEM MARS 5 XPRESS microwave at 1600 W for 45 min before being allowed to cool. Digests were then washed into individual 10 ml volumetric flasks and diluted to mark with ultrapure Millipore Milli-Q water. For an assessment of digestion efficacy and analytical accuracy, a seaweed reference material (*Fucus vesiculosus*, ERM-CD200; certified for As, Cd, Cu, Hg, Pb, Se and Zn) was digested in triplicate likewise.

Seaweed digests were analysed for elements that had been detected by XRF using a collision cell-ICP-MS (Thermo X-series II, Thermoelemental, Winsford, UK) with a concentric glass nebuliser and conical spray chamber. RF power was set at 1400 W and coolant, auxiliary, nebuliser and collision cell gas flows rates were 13 L Ar min^{-1}, 0.70 L Ar min^{-1}, 0.72 L Ar min^{-1} and 3.5 ml 7% H_2 in He min^{-1}, respectively. The instrument was calibrated externally using four standards prepared by dilutions of a QC 26 multi-element solution (CPI International, Amsterdam) in 0.1 M HNO_3, and internally by the addition of 100 μg L^{-1} of In and Ir to all samples and standards. Data were acquired over a dwell period of 10 min, with 50 sweeps per reading and three replicates.

2.4. Presentation, quality and analysis of data

Spectra arising from the XRF analyses were quantified by fundamental parameter coefficients to yield elemental