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The potential for kelp manufacture to lead to arsenic pollution of remote Scottish islands

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Abstract

Burning seaweed to produce kelp, valued for its high potash and soda content, was formerly a significant industry in remote coastal areas of Scotland and elsewhere. Given the high concentrations of arsenic in seaweeds, up to 100 mg kg^{-1}, this study investigates the possibility that the kelp industry caused arsenic contamination of these pristine environments. A series of laboratory-scale seaweed burning experiments was conducted, and analysis of the products using HPLC ICP-MS shows that at least 40% of the arsenic originally in the seaweed could have been released into the fumes. The hypothesis that the burning process transforms arsenic from low toxicity arsenosugars in the original seaweeds (*Fucus vesiculosus* and *Laminaria digitata*) to highly toxic inorganic forms, predominantly arsenate, is consistent with As speciation analysis results. A field study conducted on Westray, Orkney, once a major centre for kelp production, shows that elevated arsenic levels (10.7 ± 3.0 mg kg^{-1}, compared to background levels of 1.7 ± 0.2 mg kg^{-1}) persist in soils in the immediate vicinity of the kelp burning pits. A model combining results from the burning experiments with data from historical records demonstrates the potential for arsenic deposition of 47 g ha^{-1} $year^{-1}$ on land adjacent to the main kelp burning location on Westray, and for arsenic concentrations exceeding current UK soil guideline values during the 50 year period of peak kelp production.

Keywords: *Laminaria digitata*; *Fucus vesiculosus*; Seaweed; Orkney; Contamination

1. Introduction

In the Northern and Western Isles of Scotland and elsewhere, the drying and burning of seaweeds to produce kelp was a significant industry in the 18th and 19th centuries (Kenicer et al., 2000). Kelp is rich in potash and soda and was used in the manufacture of glass and soap, and for bleaching linen.

From 1764–1772, an estimated 4892 tonnes of kelp were produced annually in Scotland, of which 93% came from Orkney and the Western Isles (Thompson and Graham, 1978; Thompson, 1983). Annual production on Orkney during the peak production period of 1770–1820 was between 2000 and 3000 tonnes (Thompson, 1983). Assuming that 24 tonnes wet weight of seaweed is needed to produce 1 tonne of kelp (Darwin, 1996), approximately 60 000 tonnes of seaweed per year would have been gathered on Orkney at this time.

Francesconi and Edmonds (1997) reviewed total arsenic measurements in various marine algae. Mean concentrations (dry weight) ranged from 10 to 62 mg kg^{-1} in brown algae, 2–19 mg kg^{-1} in red algae and 2–16 mg kg^{-1} in green algae. Feldmann et al. (2000) reported dry weight concentrations of 24.7 ± 3.9 mg kg^{-1} in *Fucus vesiculosus*, 22.2 ± 3.7 mg kg^{-1} in *Ascophyllum nodosum*, and 72.1 ± 0.3 mg kg^{-1} in *Laminaria digitata*. Castlehouse et al. (2003) reported similar results for *F. vesiculosus* and *L. digitata*, at 25 ± 4 mg kg^{-1} and 74 ± 2 mg kg^{-1} respectively. All the above mentioned species were used to produce kelp. *Laminaria* species are the most abundant seaweeds in the relevant coastal areas (Fuller, 1999).

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More than 90% of the arsenic in *F. vesiculosus* and *L. digitata* is in the form of arsenosugars (Tukai et al., 2002; Castlehouse et al., 2003; Šlejkovec et al., 2005). Minor amounts of arsenate and trace quantities of monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) have also been reported (Francesconi and Edmonds, 1997).

Arsenic toxicity is strongly dependent on the species of arsenic present (Cullen and Reimer, 1989). Inorganic species are more toxic than organic species such as arsenosugars and arsenobetaine. Trivalent forms are more toxic that their pentavalent counterparts (B'Hymer and Caruso, 2004). Laparra et al. (2004) reported that when seaweed is cooked, some of the arsenosugars are converted to inorganic species.

To investigate the potential for kelp manufacture to cause arsenic pollution, it is necessary to examine what happens to the arsenic present when seaweed is burned. In this study, a series of seaweed burning experiments were carried out, and the products of the experiments were analysed for total As and As species. These data were combined with the statistics on the scale of the kelp industry and relevant environmental data to model the nature and extent of the hypothesised arsenic pollution. To reflect the likely range of conditions in the kelp kilns, three different types of experiments were conducted: pyrolysis of raw seaweed, burning of the seaweed with the aid of heather, and heating in a furnace at 800 °C. Two types of seaweed, *L. digitata* and *F. vesiculosus* were used in the experiments.

It is possible that pollution from the former kelp industry is still present in the form of elevated soil arsenic concentrations in areas where kelp burning was prevalent. To test this hypothesis, a soil sampling survey was conducted on Westray, Orkney.

2. Materials and methods

2.1. Seaweed collection and preparation

Approximately 20 kg (wet weight) of *F. vesiculosus* and 15 kg (wet weight) of *L. digitata* were collected from the rocky shoreline at Cowie, north of Stonehaven, Aberdeenshire, Scotland, on 30 April 2005. The *F. vesiculosus* was cut from the rocks located midway between the high and low water marks, and the *L. digitata* was gathered from rock pools around the low water mark. Excess seawater was shaken off, and the material was washed with tap water and laid out in shallow trays to air dry. After 3 days, the trays of seaweeds were relocated to a constant temperature (40 °C) room and turned every few days until dry and brittle, then broken into small fragments (1–2 cm) and removed to the laboratory. Prior to use in the experiments the seaweeds were oven dried overnight at 70 °C then ground to smaller (<3 mm) particles using a mortar and pestle.

2.2. Heather collection and preparation

Approximately 10 kg of heather (*Calluna vulgaris*) were collected from Durris Forest, Deeside, Aberdeenshire, Scotland, on 25 May 2005. The heather was broken up into fragments 1–5 cm long, then oven-dried overnight at 70 °C and further broken up into 0.5–1.0 cm long fragments.

Morrisons 'Barbecue Lighting Cubes' were used to light the fires in the burning with heather experiments.

2.3. Chemicals

Nitric acid (AnalR 70% HNO_3), sulphuric acid (98% H_2SO_4) and hydrogen peroxide were purchased from Fisher Scientific. Mono-sodium arsenate ($NaHAsO_4$) and sodium arsenite ($NaAsO_2$) were purchased from Merck. Dimethylarsinic acid, DMA(V), was bought from Sigma Chemicals and monomethylarsonic acid, MMA(V), from Chem Service MC, West Chester. Indium (In) was prepared in-house from indium chloride. Rhodium (Rh) was standard solution obtained from Asfa Aesar. Aqueous ammonia solution (35% NH_3) was purchased from BDH. The certified reference material used was TORT–2 lobster heptopancreas, 21.6 ± 1.8 mg kg^{-1} As, from the National Research Council, Canada.

2.4. Determination of total arsenic concentration in raw materials

Sample preparation: for each of the raw materials, *L. digitata*, *F. vesiculosus*, and heather, the samples were prepared as follows. A 2 g (dry weight) sample of the seaweed was digested in 2 ml nitric acid for 3 h at 140 °C. De-ionised water was added to the clear digest solution to make a total volume of 10 ml. To a 1.0 g sample of this volume, 0.1 g of 1000 ng g^{-1} Indium and 8.9 g of de-ionised water were added prior to analysis.

Arsenic analysis was performed using an ICP-MS 7500 (Agilent Technologies). Appropriate quality control measures were taken to validate the analytical procedures. Instrumental limits of detection were 0.03 ng ml^{-1}. Recovery of the reference material TORT-2 (lobster heptopancreas) was $74.2 \pm 2.6\%$ ($n = 6$) of the certified value of 21.6 ± 1.8 mg kg^{-1}. Spike recovery was $92.4 \pm 2.6\%$, and blanks measured 1.2 ± 0.0 ng ml^{-1} ($n = 7$).

2.5. Burning experiments

The following experiments were carried out in triplicate:

Burning *L. digitata* (2.00 ± 0.01 g), heather (2.00 ± 0.01 g) and firelighter (0.6–0.8 g).
Burning *F. vesiculosus* (2.00 ± 0.01 g) and heather (2.00 ± 0.01 g) and firelighter (0.6–0.8 g).
Pyrolysis of *L. digitata* (2.00 ± 0.01 g).
Pyrolysis of *F. vesiculosus* (2.00 ± 0.01 g).
Heating *F. vesiculosus* (10.00 ± 0.01 g) in a furnace.
Heating *L. digitata* (10.00 ± 0.01 g) in a furnace.

A separate experiment, burning the firelighter, was conducted for reagent control.