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Modelling temporal trends of ^{137}Cs and ^{99}Tc concentrations in *Fucus vesiculosus* from the eastern Irish coastline

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ABSTRACT

Time series of ^{137}Cs and ^{99}Tc activity concentrations in the brown seaweed *Fucus vesiculosus* and seawater, gathered at three locations on the eastern Irish coastline during the period 1988–2008, have been modelled using a novel approach incorporating a variable uptake rate in the seaweed. Seasonal variations in the time series, identified using spectral analysis, were incorporated into the model which was used to determine transfer kinetic parameters and to predict ^{137}Cs and ^{99}Tc concentrations in seaweed, as influenced by levels in ambient seawater. An optimisation method combining evolutionary and grid search minimisation techniques was adopted to determine the best values for the model parameters, from which concentration factors (*CF*) and biological half-lives ($tb_{1/2}$) for ^{137}Cs and ^{99}Tc in *F.* vesiculosus were calculated. *CF* values of 170–179 and 1.1×105 l kg^{-1} (dry weight) were obtained for ^{137}Cs and ^{99}Tc, respectively, while the corresponding $tb_{1/2}$ values were 39–47 and 32 days, respectively.

1. Introduction

1.1. Seaweed as a bio-indicator

The brown algae *Fucus vesiculosus* is known to effectively concentrate radionuclides and heavy metals from seawater and, as a result, has been widely used as a bio-indicator in marine and estuarine pollution studies (Fuge and James, 1974; Germain et al., 1995; Keogh, 2006; Kershaw et al., 2005). These studies have shown that analysis of radionuclide and heavy metal concentrations in seaweed can provide an accurate picture of concentrations in the surrounding waters (Black and Mitchell, 1952; Bryan and Hummerstone, 1973; Burger et al., 2006; Carlson and Erlandsson, 1991; Morita et al., 2010; Nawakowski et al., 2004). Furthermore, concentrations in archived seaweeds have been used to hindcast trends in the discharge rate of radionuclides where there is incomplete discharge information from their principal sources (Aarkrog et al., 1995; Fievet and Plet, 2003; Raisbeck et al., 1995). The increased sensitivity that can be achieved using *Fucus* species, owes to its high concentration factor for many different pollutants. Indeed, data relating to the uptake by some common *Fucus* species of certain trace contaminants have shown *F. vesiculosus* to have the greatest degree of accumulation when compared to other members of the fucoid family (McCartney and Rajendran, 1997). A concentration factor (*CF*, l kg^{-1}), defined as the ratio of the concentration in fresh seaweed (Bq kg^{-1}) to that in filtered seawater (Bq l^{-1}), is employed to describe the degree of accumulation in seaweed relative to seawater, with *CF* values varying with different species and contaminants. For *F. vesiculosus*, *CF* values for ^{137}Cs and ^{99}Tc have been reported to be approximately 32 and 3×10^4 l kg^{-1} (wet weight), respectively (Kershaw et al., 2005).

A potential drawback of the use of bioindicators for monitoring purposes is the reported seasonality in the uptake, irrespective of water concentrations (Fuge and James, 1974; Kershaw et al., 1999; Nawakowski et al., 2004; Riget et al., 1995; Villares et al., 2002). In some cases, higher concentrations have been observed to occur during the winter months, when seaweed undergoes a period of slow growth. In *F. vesiculosus*, this effect has been reported for ^{99}Tc concentrations (Kershaw et al., 1999) and ^{54}Mn (Carlson and Erlandsson, 1991). In contrast, ^{137}Cs in *F. vesiculosus* appear to follow an opposite trend, with the radionuclide accumulating to a higher extent in the seaweed during the early summer months (Carlson and Erlandsson, 1991). Increased concentrations during the summer period have been attributed to increased contaminant levels in receptacles and new growth in the algae. It is reported that at this time, the receptacles are mature and accumulate Cl-linked monovalent cations, such as Na^+ and K^+ (Munda and Hudnik, 1986), which could also explain the observed increase in the uptake of the Cs^+. While divalent heavy metal ions such as Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+} and Hg^{2+} are taken up by passive transport (Davis et al., 2003), there is some uncertainty as to whether K^+ and Cs^+ ions are taken into algal cells by active transport, by an electropotential or a Donnan system (Lewin, 1962).

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In this study, time series of ^{137}Cs and ^{99}Tc activity concentrations in *F. vesiculosus* and seawater (affected by discharges from Sellafield), gathered at different sampling locations on the eastern Irish coastline in the period 1988–2009 were measured and their seasonality analysed. A novel modelling approach, taking into account a variable uptake rate by the seaweed, was then adopted with a view to (i) identifying any possible seasonality in the uptake of these radionuclides; and (ii) calculating appropriate values for the respective concentration factors (*CF*) and biological half-lives ($tb_{1/2}$).

2. Materials and methods

2.1. Sampling and analysis

Sampling of seawater and seaweed was undertaken by staff of the Radiological Protection Institute Ireland (RPII) as part of their programme of radioactivity monitoring of the Irish marine environment. Adult individuals of *F. vesiculosus*, as well as seawater samples, were collected from three separate locations (Greenore, Balbriggan and Bull Island, see map in Fig. 1) over a period of 20 years from 1988 to 2008 inclusive. Seaweed samples were collected on a regular basis, typically once a month per location, while seawater samples were collected less frequently, typically every 2–3 months per sampling site. Fucus individuals, having reached the Gametophyte stage, were collected at low tide and washed in nearby seawater to remove any extraneous material. Samples (250 g) were then oven dried at 80 °C for 24 h, ground, and thoroughly homogenised.

For seawater, ^{137}Cs was separated from the seawater (50 l) using ASG, a caesium exchanger consisting of silica gel impregnated with ammonium molybdophosphate. The water was initially filtered through a (0.45 μm) filter and adjusted to pH 2 with nitric acid prior to passing it through ASG exchange resin. The ASG resin was then placed in a well-defined and calibrated geometry prior to radiometric measurement (Baker, 1975).

^{137}Cs levels in each sample were determined by high-resolution gamma spectrometry using an n-type germanium detector with relative efficiency of 30% and resolution of 1.70 keV (FWHM) at 1.33 MeV. The counting times for the seawater and seaweed samples were typically 1 and 3.5 days, respectively. ^{99}Tc concentrations in seaweed and ambient (filtered) seawater were analysed using a radiochemical separation technique in accordance with the method described by Harvey et al. (1991), followed by beta spectrometry using a gas-flow proportional counter.

2.2. Analytical and optimisation techniques

2.2.1. The Lomb periodogram

Spectral analysis of each time series was achieved through use of the Lomb–Scargle periodogram (Lomb, 1976; Scargle, 1982), a spectral technique for detecting periodicities in unevenly sampled time series. The periodogram performs a general linear least squares regression of the data to a sine/cosine series of different frequencies. The Lomb normalised periodogram, with spectral power dependent on angular frequency with $\omega \equiv 2\pi f > 0$ and frequency f, is defined by:

$$P_N(\omega) \equiv \frac{1}{2\sigma^2}\left\{\frac{\left[\sum_j (h_j-\bar{h})\cos(\omega(t_j-\tau))\right]^2}{\sum_j \cos^2(\omega(t_j-\tau))}+\frac{\left[\sum_j (h_j-\bar{h})\sin(\omega(t_j-\tau))\right]^2}{\sum_j \sin^2(\omega(t_j-\tau))}\right\} \tag{1}$$

where τ is defined by the equation:

$$\tan(2\omega\tau) \equiv \frac{\sum_j \sin(2\omega t_j)}{\sum_j \cos(2\omega t_j)}, \tag{2}$$

where σ^2 is the variance of $(h_j - \overline{h})$, and $\overline{h}$ and h_j are defined to be the mean concentration value and the individual concentration values measured at time t_j, respectively.

The periodogram is a normalised function due to the inclusion of σ^2, with the significance of the frequencies exhibiting an exponential probability distribution. The probability that $P(\omega)$ will be

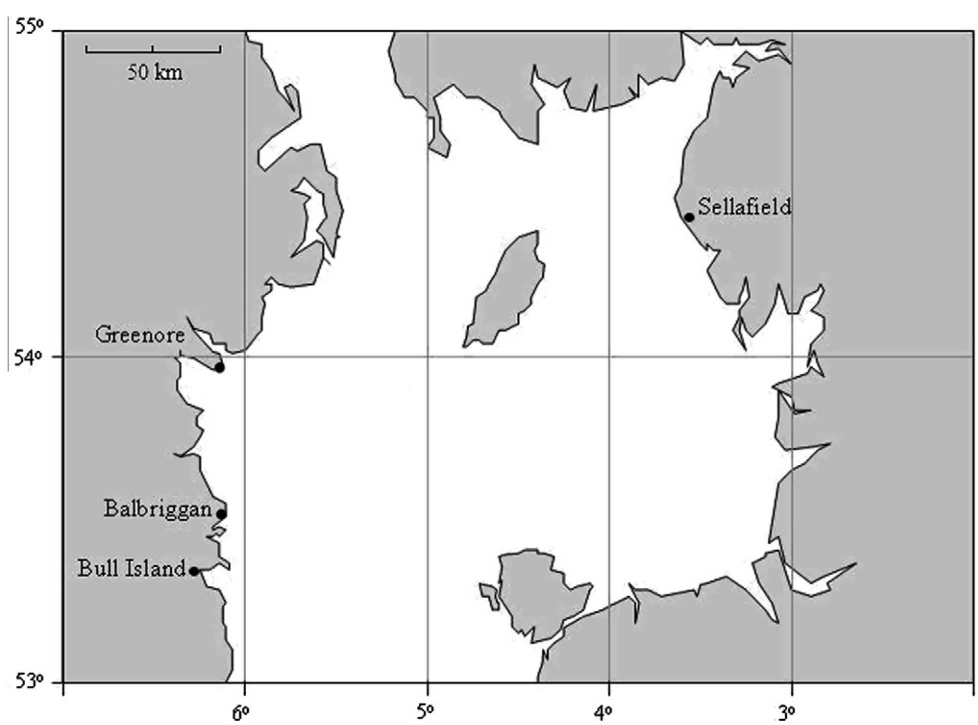

Fig. 1. Sampling locations on the east coast of Ireland (Balbriggan, Bull Island and Greenore,) of *Fucus vesiculosus* and ambient seawater over a period of 20 years from 1988 to 2008, inclusive.