DETERMINATION OF γ-RAYS EMITTING RADIONUCLIDES IN SURFACE WATER: APPLICATION OF A QUANTITATIVE BIOSENSING METHOD

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SUMMARY

A quantitative biosensing method has been developed for the determination of γ-rays emitting radionuclides in surface water. The method is based on the concept that at equilibrium the specific radioactivity in the biosensor is equal to the specific radioactivity in water. The method consists of the measurement of both the radionuclide and the related stable isotope (element) in the biosensor and the determination of the element in water.

This three-way analysis eliminates problems such as unpredictable biosensor behaviour, effects of water elemental composition or further abiotic parameters on accumulation levels: what remains is the generally high enrichment (bioaccumulation factor BCF) of elements and radionuclides in the biosensor material. Using water plants, the method is shown to be three to five orders of magnitude more sensitive than the direct analysis of water.

INTRODUCTION

Radionuclides are present in surface waters in very low concentrations, with values which may go down to the μBq/L levels (Coughtrey & Thorne 1983, Momoshima *et al.* 1993). For analysis, it is necessary to sample large water volumes, followed by complex chemistry in the laboratory. In routine monitoring, chemical handling is generally reduced to a minimum to increase sample through-put: γ-rays emitting radionuclides are often measured directly in Marinelli-geometry (Suzuki *et al.* 1984, De Meijer 1987, Eggink *et al.* 1993). The absence of any enrichment step in the analytical procedures results in a limited sensitivity and, thus, does not permit low-

level analysis.

The application of a bio-organism which continuously accumulates radionuclides in the field situation may permit relatively fast and easy field sampling, should reduce the laboratory chemistry and should enable the performance of a sensitive analysis. However, the commonly reported drawback of any biosensing method is that the bio-organism is considered as a-specific, shows ill-defined accumulation behaviour, and exhibits variable responses towards a range of environmental conditions (light, temperature, water matrix or other trace elements etc.) (Beaugelin-Seiller *et al.* 1994, Kryshev & Sazykina 1994).

The present paper demonstrates the applicability of water plants as sensitive and *quantitative* biosensors for radionuclides in surface water. The proposed method consists of a three-way analysis, which eliminates problems such as unpredictable biosensor behaviour or the effects on uptake processes of the water elemental composition.

MATERIALS AND METHODS

General.

The proposed method consists of the analysis of radionuclides and related stable isotopes (elements) in the biosensor, and the determination of the elements in water (Wolterbeek & Van der Meer 1995).

Based on the known specific radioactivity in the biosensor, the water element concentration can be used directly to calculate the water radionuclide concentration. Here, the element and the related radionuclide are considered to show similar enrichment (BCF, or bioaccumulatio factor) in the biosensor material.

Plant material.

Samples were taken of floating *Azolla filiculoides* Lamk., *Spirodela polyrrhiza*, and of the fully submerged *Ceratophyllum demersum* L. water plants. After sampling, the plants were placed in cotton bags, and adhering water was removed by centrifugation in a spin-drier. The plants were dried and eventually milled (FRITSCH pulverisette 14 rotor speed Mill), homogeneized and stored in closed 1 L volume Marinelli beakers.

Water.

Ditch water was sampled in 10 L polyethylene bottles, fast-filtered to remove floating and/or large particles, and fine-filtered over 2 μm polycarbonate (Wolterbeek & Van der Meer 1995). After acidification, 5 L were freeze-dried, and 1 L volumes were stored in closed Marinelli beakers.

Analysis.

Elemental analysis was carried out by instrumental neutron activation analysis (INAA) (Blaauw 1993) and by ICP-MS (Inst. Nucl. Sci., Gent, Belgium).
Gamma-rays emitting radionuclides were determined using a lead-shielded planar Ge-detector (Marinelli-geometry: plants, water) or a well-type Ge(Li) detector (freeze-dried water) (Wolterbeek & Van der Meer 1995).

RESULTS AND DISCUSSION

Elements.

Fig. 1 shows the enrichment factors (BCF) in *Azolla* (similar to *Spirodela*, results not shown) and in *Ceratophyllum*, for a variety of elements. The BCF-values range from about 100 L/kg for Li, Ca or Na to 1.2 10^5 L/kg for Fe and Mn (the latter values both found in *Ceratophyllum*). In general, the BCF-values observed correspond to values found elsewhere for duckweed and other water plant species (Van Wijk 1989, Kwan & Smith 1991, Tripathi & Chandra 1991, Huebert & Shay 1992).

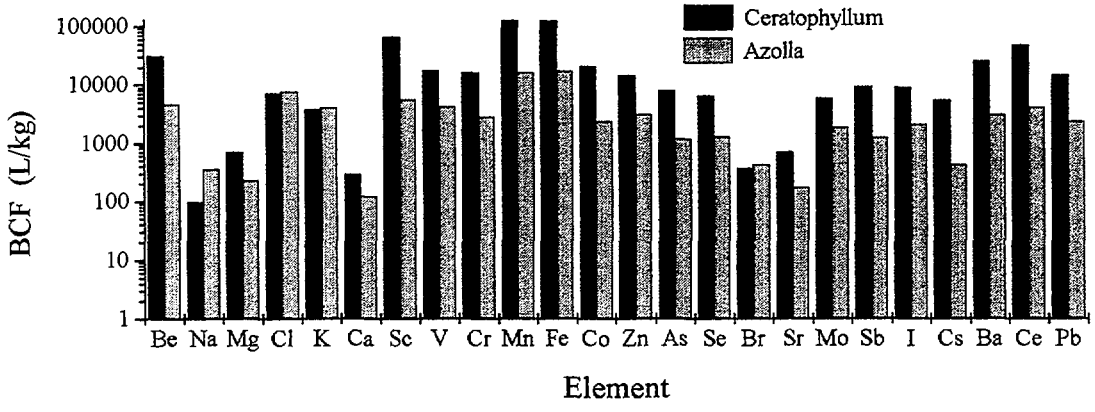

Fig. 1 Bio-concentration factors for various elements in *Azolla* en *Ceratophyllum*.

Radionuclides.

Fig. 2 gives an example of γ-ray spectra, obtained from Marinelli-geometry measurements of the biosensor plants. For measurements, about 200 to 500 g dried plant mass was weighed in the Marinelli beakers.

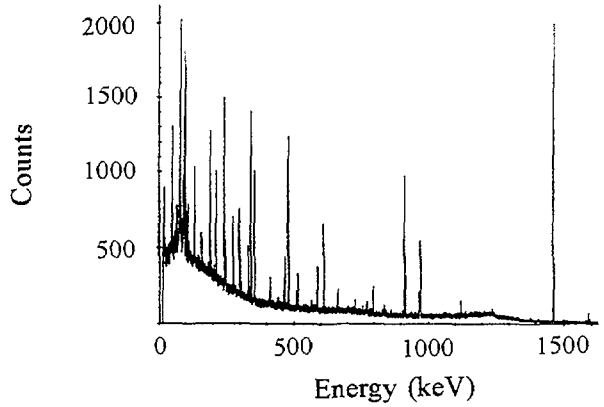

Fig. 2

Gamma-ray spectrum obtained by measuring 500 g of *Ceratophyllum*.

Based on combined BCF-values and outcomes of γ-ray spectra, differences in sensitivity could be calculated between direct analysis of water and the biosensing method. Fig. 3 shows values for the limits of detection, expressed in Bq/L, based on 24 h measurements in Marinelli geometry. The data show that application of the water plants results in improvements in sensitivity up to five orders of magnitude.

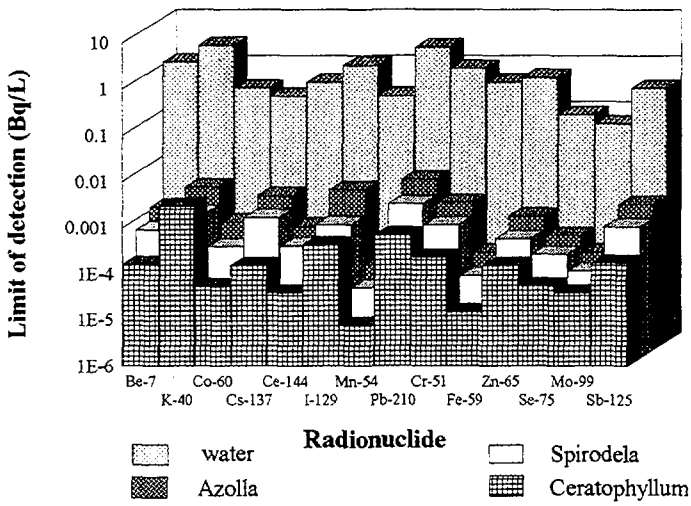

Fig. 3

Comparison of sensitivities obtained when using *Azolla*, *Ceratophyllum*, *Spirodela* or direct water analysis.

Quantitative biosensing.

Fig. 4 shows comparisons in outcomes between the direct analysis of water and the biosensing method, the latter using both *Azolla*, *Spirodela* and *Ceratophyllum*.

For ^{40}K and ^{137}Cs, all outcomes correspond. For ^{212}Pb, the direct analysis of water did not yield any value, due to the limited analytical sensitivity. The

biosensing results, although somewhat variable, all indicate about 5-10 mBq/L ^{212}Pb levels in water. For ^{7}Be, there is a clear difference between the outcomes of the direct analysis of water and of *Ceratophyllum* on the one hand, and of the outcomes obtained with *Azolla* and *Spirodela* on the other. Apparently, the *floating* water plants do not accumulate ^{7}Be only from the water phase, but also from atmospheric deposition (Gaffney *et al.* 1994), up to about 85 % of their total content of ^{7}Be. In this respect, floating water plants may be seen as indicators for atmospheric ^{7}Be rather than as biosensor organisms for ^{7}Be in surface water. The data for the fully submerged *Ceratophyllum* plants, however, fully correspond to the outcomes of the direct analysis of water.

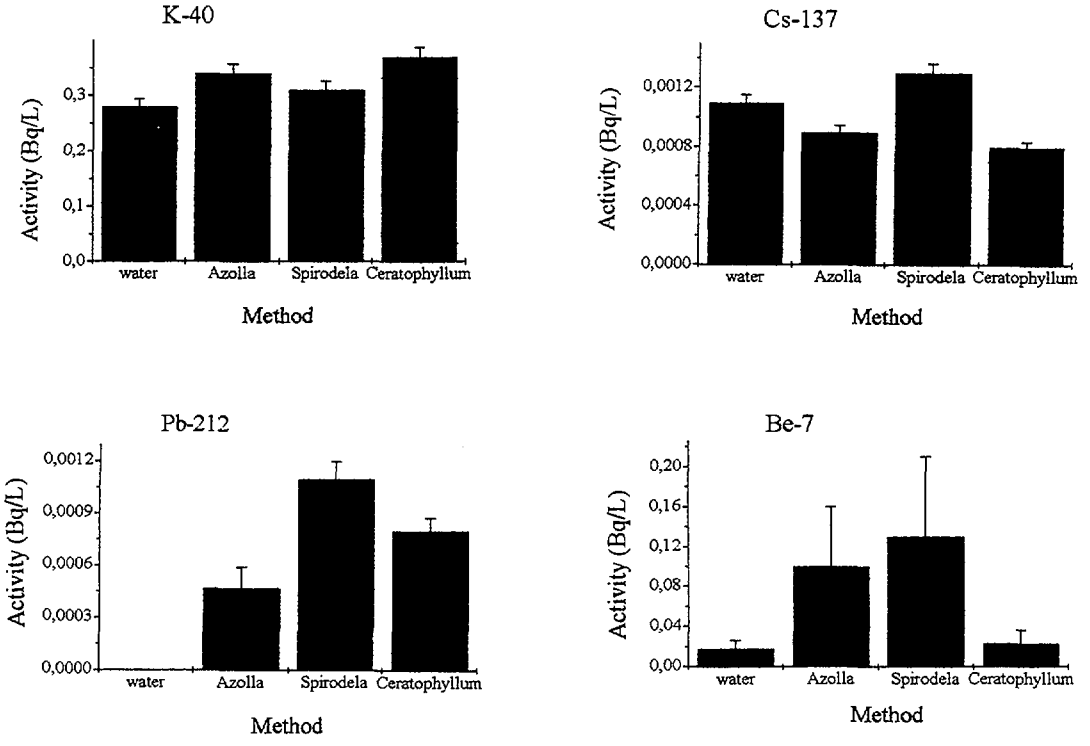

Fig. 4 Comparison of outcomes using *Azolla, Ceratophyllum,Spirodela* or direct water analysis.

Time resolution.

The biosensor organism should reflect the levels of the elements and radionuclides in water, which makes that it should respond rapidly to changes in concentrations of both elements and radionuclides. The response-rate should be regarded as fast, *relative* to the rate at which the changes take place. Fig. 5 presents preliminary

results of kinetic experiments with $^{57,60}Co$ and $^{134,137}Cs$ radionuclides, indicating laboratory response-times in duckweed in the order of 10-20 days.

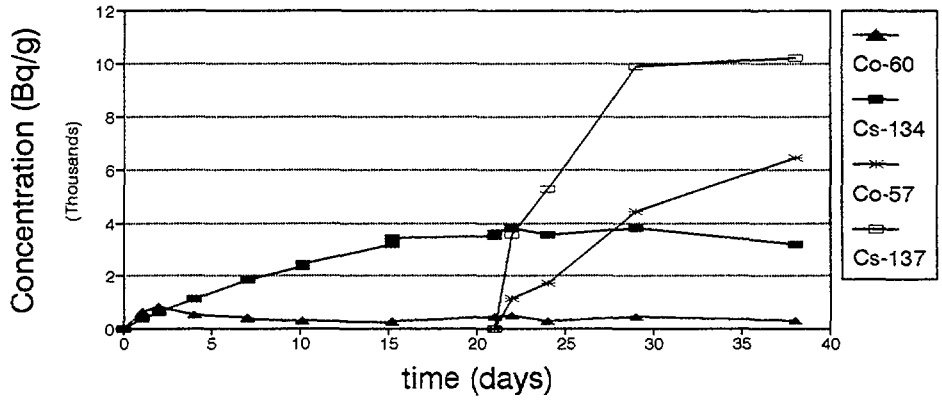

Fig. 5 Response of Duckweed to addition of Co and Cs.

These response-times agree with results obtained by Kwan & Smith (1991) for uptake of Cd and Tl in *Lemna* species. Apart from sudden and large releases (*e.g. Chernobyl*), the dynamics of changes in environmental concentrations of elements and radionuclides is relatively slow and should be presented in terms of years rather than days (Dehut *et al.* 1989, Fesenko *et al.* 1995). Based on the above, the proposed biosensing method may not only be regarded as sensitive but also as quantitative.

PROSPECTS

The present results obtained with water plants sampled from ditch water indicate the potential of the use of biosensor organisms for monitoring radionuclides in surface water in the context of the concept of specific radioactivity. *Quantitative* results are obtained by the decribed *three*-way analysis. Reliable *relative* results may be obtained by determination in the biosensor of the specific radioactivity: here, the radioactivity signal is simply normalized by the simultanuous measurement in the biosensor of the related stable isotope (element). The method may be applied to a variety of biosensor organisms: these include both plants and animal organisms. Future use may lead to a better understanding of the diffuse spread of radionuclides in surface waters.

Note: ***Parts of this work have been submitted for publication in the Journal of Environmental Radioactivity.***

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