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Temporal changes in elemental composition in decomposing filamentous algae (*Cladophora glomerata* and *Pilayella littoralis*) determined with PIXE and PIGE

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ABSTRACT

Particle-induced X-ray emission and particle-induced gamma-ray emission spectrometry were successfully applied in a study of the elemental composition of decomposing filamentous algae. Fresh brown (*Pilayella littoralis*) and green (*Cladophora glomerata*) algal materials were placed in cages at 4 m depth in a water column of 8 m in the Archipelago Sea, northern Baltic Sea. Every second week decaying algae were sampled from the cages to allow measurements of changes in the elemental compositions. In the study of the elemental losses the concentrations were compensated for the mass reduction. The results show that sulphur, chlorine and partly potassium were lost during decomposition of *P. littoralis* and *C. glomerata*. Most of the other elements studied were recovered in the remaining algal mass. Special attention was paid to sorption and desorption of elements, including metal binding capacity, in the decaying algal materials. The affinity order of different cations to the two algal species was established by calculation of conditional distribution coefficients, D'_M. For instance for *P. littoralis* the following series of binding strength (affinity) of cations were obtained: Al > Ti > Fe ≫ Mn > Ni, Cu > Ba, Cr, Zn ≫ Rb > K, Sr > Pb ≫ Ca ≫ Na > Mg. Notably is that the binding strength of strontium was more than 10 times higher for *P. littoralis* than for *C. glomerata*. Due to their high binding capacity and good affinity and selectivity for heavy metal ions these algae have great potential as biological sorbents. Large variations in elemental content during decomposition complicate the use of algae for environmental monitoring.

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1. Introduction

Large-scale eutrophication has promoted growths of annual filamentous algae in coastal areas world-wide (Cloern, 2001; Fletcher, 1996). When large biomasses of algae detach at the end of their lifecycles, they either get washed up on the shore or gather at the sea bottom resulting in algal mats of varying size, density, composition and condition. Drifting macroalgae are common in all parts of the Baltic Sea and large occurrences have been recorded in the Finnish Archipelago Sea with continuous drifting algal mats exceeding 30 ha at >20 m depth (Vahteri et al., 2000). As the detached algal material slowly decomposes available oxygen is consumed, resulting in large anoxic areas, where macroscopic animal and plant species cannot survive (Bonsdorff, 1992). Much of the algal degradation takes place under anoxia where anaerobic and sulphur bacteria are the major decomposers (Fenchel et al., 1998). The degradation process of filamentous algae is highly temperature dependent and also the impact of sediments and its compounds promote algal decay (Salovius and Bonsdorff, 2004). However, it is unknown how the chemical degradation takes place and which elements accumulate in the decaying algal material.

The brown alga *Pilayella littoralis* (L.) Kjellm. and the green alga *Cladophora glomerata* (L.) Kütz are two of the most common macroalgal species in the northern Baltic Sea and have been used in this study. *C. glomerata* is also considered as the most proper bioindicator of heavy metals (Chmielewská and Medved', 2001), and it has a high and constant capacity to take up metals from aquatic environments (Keeney et al., 1976). Vymazal (1987) has studied the uptake of zinc by *C. glomerata* in the pH region 5.5–8.5 and found it to be very rapid and to increase with rising pH. Algae or more precisely alginate in brown algae have received attention due to their potential therapeutical use in connection with overdoses of strontium-90 (Haug and Smidsrød, 1967). The brown alga (*P. littoralis*) has also been tested as biosorbent for preconcentration in trace metal analysis (Carrilho et al., 2003).

The elemental concentrations can be measured with several instrumental methods (Willard et al., 1988). Wet chemical methods

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like inductively coupled plasma optical emission spectrometry (ICP-OES) (Carrilho et al., 2003), graphite furnace atomic absorption spectrometry (GFAAS) (Carrilho et al., 2003), inductively coupled plasma mass spectrometry (ICP-MS) have mostly been used in the chemical analysis of algae. However these methods require time consuming digestion of the samples, with risks for contamination. Particle induced X-ray emission (PIXE) offers reliable analyses with a minimum of sample preparation (Johansson et al., 1995). The light elements are problematic to determine with PIXE because of the absorption of X-rays in air, detector window etc. However, many of these elements are assessable by measuring the gamma radiation emitted from the nuclei during particle bombardment. The determination of the total nitrogen content in thick samples with this particle induced gamma emission technique (PIGE) requires that the particle irradiation is performed in a nitrogen free atmosphere.

The aims of this study were to investigate, which harmful elements accumulate in the decaying macroalgae. This study will contribute to a better understanding of the reactions and processes governing the uptake of elements by algae. Furthermore the analytical methods may be used as tools for developing monitoring programmes to assess marine environmental status according to EU legislation (Marine Strategy Framework Directive, Water Framework Directive).

2. Materials and methods

2.1. Sampling and sample preparation

Two filamentous algal species were used in our study, the cold-water brown alga *Pilayella littoralis* and the warm water green alga *Cladophora glomerata*, since they are both key species in drifting algal mats in the Northern Baltic Sea (Vahteri et al., 2000). We studied the algal decomposition by collecting fresh algae from the shore, cleaning them from macrofauna and rinsing them to get rid of sediment particles. The cleaned algae were inserted into cages, 20 cm diameter and 20 cm high. All sides of the cages consisted of a net with mesh size of 1.2 mm × 2 mm to allow water exchange and prevent conditions inside to become hypoxic. The cages were filled by 1 kg wet weight of *P. littoralis* in early summer and by 1 kg wet weight of *C. glomerata* later in the season. The cages (n = 3 for each algal species) were placed at 4 m depth in the water column at a distance of 400 m from the nearest shore in a semi-exposed area outside Själö Island in the Archipelago Sea in the southwest of Finland (Fig. 1., 60°14′ N, 21°59′E). The bottom substrate consisted of sand and silt and the water depth was 8 m. As the experiment was initiated, fresh algae were taken as reference samples to give initial concentrations. Every second week algae were sampled from the cages to allow us to temporary measure changes in the element composition during algal decay. The *P. littoralis* biomasses decreased slower than the mass of *C. glomerata*, due to the colder water temperatures in the beginning of summer. Therefore, four sampling occasions were possible from the *P. littoralis* experiment and only three from the *C. glomerata* experiment. A sea water sample was later collected (28 July 2009) from the same site.

During sampling, the cages were carefully lifted and a small amount of alga (2–5 g dry weight) was retrieved from each cage and put in separate plastic bags. In laboratory, macro fauna that had immigrated from the surrounding water body (Salovius and Bonsdorff, 2004) were picked off and the algal samples were dry freezed and stored in a freezer. The dried and ground algal samples were pressed to pellets prior to PIXE and PIGE analysis.

2.2. Analytical methods

In the PIXE analysis the samples were irradiated in air for about 10 min each with an external 3 MeV proton beam from the Åbo Akademi MGC-20 cyclotron. The integrated charge on the sample was determined from light induced in the beam path in air (Lill, 1999). The emitted X-rays were measured with an intrinsic germanium planar detector. The GUPIX software package was used to calculate the elemental concentrations from the obtained spectra (Maxwell et al., 1999). The calibration was checked at each run by analyzing a pressed pellet of the certified granite standard G2 (USGS). A pellet of spectroscopically pure graphite was also irradiated at the beginning of each run to determine possible background interferences. The precision and accuracy of the method have been evaluated earlier by our group by analysing well-known certified reference materials (Harju et al., 1997; Lill et al., 1999; Lill et al., 2011).

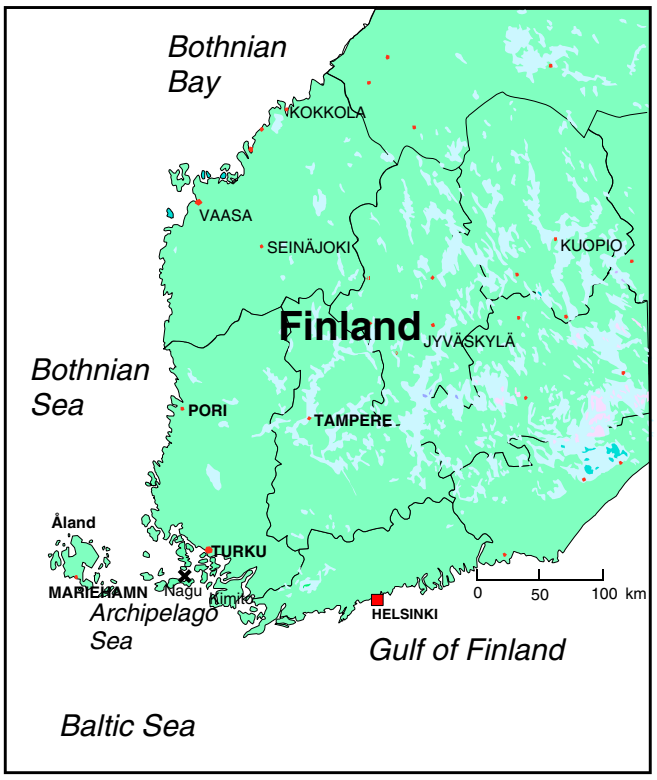

Fig. 1. The cages (n = 3 for each algal species) were placed at 4 m dept in a water column of 8 m at a distance of 400 m from the shore in the Archipelago Sea. The sampling site is marked with an x on the map.

The PIGE analysis was performed in a helium atmosphere to avoid interference from nitrogen in air. The proton energy incident on the sample was 4.2 MeV (Lill et al., 2007). The ion beam was collimated to a diameter of 2.5 mm and extracted out of the cyclotron vacuum system through a 4 μm thick nickel foil (Goodfellow Cambridge Limited, NI000220). A helium gas flow of 10 cm^3/min was used during the irradiations. The gas chamber was flushed prior to the irradiation. The emitted radiation was measured with an EG&G ORTEC high-purity germanium (HPGe) coaxial detector located 22 mm behind the flange of chamber. The obtained spectra were analysed for peak areas off line using SAMPO90 (Aarnio et al., 1988). The peaks from the nickel foil at 1454 keV were used for charge normalisation of the peak areas. A pressed pellet of KNO_3 was used for calibration of nitrogen. The method was evaluated using different certified reference materials (CRMs, Table 1). Al, P and Na were calibrated using biological CRMs (Saarela et al., 2000). The spectroscopic background was determined by irradiating a pellet of pure graphite.

2.3. Definition of conditional distribution coefficients

The conditional distribution coefficient, D'_M, is an important concept in two phase equilibria. It describes the distribution of a metal

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