Chemical Speciation Analysis and Environmental Behaviour of $^{127}$I and $^{129}$I

This thesis deals with chemical speciation analysis and behaviour of the anthropogenic radioisotope $^{129}$I as well as stable iodine $^{127}$I in environmental samples such as freshwater, seawater, soils, sediments and seaweed. The behaviour and chemical speciation of iodine ($^{127}$I and $^{129}$I) in environmental samples are very complex and strongly dependent on several factors, such as water/soil/sediment chemistry, seaweed type, different pH, Eh, quantity and quality of organic matter, microbiological activity as well as differences in contaminant origin. The $^{129}$I isotope, where the main inventory has been present in the biosphere for a relatively short time, may not show the same behaviour as the stable $^{127}$I isotope. The present study illustrates this. Chemical speciation analysis of $^{127}$I and $^{129}$I as iodide, iodate and total inorganic iodine in seawater samples from the Baltic Proper, Skagerrak and Kattegat has been carried out. The general trend in variability of the iodide and iodate speciation of the two iodine isotopes is, to a large extent, linked to environmental conditions. The important findings of this study are that the reduction of iodate and oxidation of iodide in Skagerrak and Kattegat may be a slow process while along the Baltic Sea surface water reduction of iodate is a relatively fast process. Although suboxic or anoxic condition are encountered in some of the Baltic Sea deep basins, the concentration of $^{129}$IO$_3^-$ increases with water depth indicating that the reduction of iodate in the oxygen deficient bottom water of the Baltic Sea is a slow process. Iodine chemical speciation analysis (as iodide, iodate and total iodine including inorganic and organic iodine species) in lake water samples collected from Denmark and southern Sweden has been carried out. Destruction of organic iodine was performed by alkaline oxidation using NaOH – NaClO at 1000°C and anion exchange chromatography was used for separation of iodide and iodate. Iodine-129 concentrations in the lakes ranged from 1.3 – 12.8 x10$^{-1}$ atL and show elevated concentrations in lakes located in southwest Jutland (Denmark), near the North Sea. Except the Skærsø Lake, were the organic iodine – 127 accounts for 50% of the total iodine, iodide (both 129I and 127I) is the predominant species in surface water of the studied lakes.

An investigation was conducted in order to quantify the total aquatic iodine ($^{129}$I and $^{127}$I as inorganic and organic iodine) from fresh water and seawater samples by adsorption onto activated charcoal and DEAE 32 cellulose followed by alkaline digestion or combustion. The results show that iodide from freshwater samples can easily be adsorbed onto activated charcoal. The sorption was not affected by the pH. The absorption capacity of iodate is low and reduces quickly when its concentration increases. Compared with activated charcoal, DEAE 32 cellulose showed a lower adsorption capacity of inorganic and organic iodine species. Adsorption of iodine species onto activated charcoal and DEAE 32 cellulose from seawater samples shows that only about 10% of the total iodine in seawater can be adsorbed onto those materials. Adsorption of iodine species from water samples onto activated charcoal/DEAE is not a suitable method for quantifying the total iodine in freshwater and seawater.

An investigation was conducted in order to decompose organic iodine using K$_2$S$_2$O$_8$ in water samples for developing a method for quantification of aquatic organic iodine ($^{129}$I and $^{127}$I). The results show that iodine was quantitatively removed even when the concentration of organic iodine compounds in the studied sample was very high. Due to this, oxidation of iodine organic matter by using K$_2$S$_2$O$_8$ followed by reduction of iodine species and precipitation with silver can be a potential method for determination of total iodine in fresh water samples. An improvement was made of the method for $^{127}$I and $^{129}$I speciation analysis in soil and sediment samples involving the extraction and fractionation of organic matter. The improved method was further used for the partitioning of $^{127}$I and $^{129}$I in marine sediments and soils. Sequential extraction results point out that partitioning of $^{127}$I and $^{129}$I within the organic fraction in soil and marine sediments is controlled by pH conditions where pH values below 5.0-5.5 promote occurrence of $^{127}$I and $^{129}$I in the humic acid, while at pH > 6 the partitioning was in the fulvic acid fraction. Anoxic conditions seemed to increase the mobility and availability of iodine compared to oxic, while suboxic conditions (soils) reduced the availability of the water soluble fraction compared to the subaqueous (marine) one. The distribution of $^{129}$I/$^{127}$I values differed significantly between phases and samples, indicating that equilibrium with stable iodine have not yet been reached for a large fraction of the released $^{129}$I. This means that geochemical models based on stable iodine behavior may not necessarily be able to predict the present behavior of I-129.

Concentrations of $^{129}$I and $^{127}$I in archived Fucus Vesiculosus samples collected between 2002 – 2010 at Romø (German Bight), Klint (Kattegat) and Bornholm were analysed. Since previous investigations have shown that iodine speciation differ between the sites a comparison between $^{129}$I/$^{127}$I ratios in seaweed relative to water at the three sites were done in order to evaluate if uptake was independent on speciation. The $^{129}$I/$^{127}$I (seaweed) relative $^{129}$I/$^{127}$I (seawater) were found to be 0.5 for the North Sea (2005), 0.7 (2006) for Southern Kattegat and 0.97 (2007) for Bornholm. In spite of the very different iodine speciation at the three sites the concentration ratio seaweed to water is more or less the same indicating that Fucus Vesiculosus can be used as a bio-indicator for iodine-129 in the marine environment. The results shows however that iodide is somewhat more efficient accumulate than iodate in Fucus. A rapid on-line HPLC-ICP-MS method for direct speciation analysis of $^{127}$I (as iodide and iodate) in water samples was developed. The method was further used for the speciation analysis of $^{127}$I in freshwater and seawater (following dilution). The results demonstrate that the on-line HPLC – ICP - MS method developed in this study is reliable and efficient for accurate assay for speciation analysis of stable iodine in water samples. Due to the low concentrations of $^{129}$I in the environment the HPLC-ICPMS method cannot be applied for speciation analysis of this isotope in environmental samples but can be applied for water samples highly contaminated with $^{129}$I.