Name of research institute or organization:

Eawag, Department Water Resources and Drinking Water, Environmental Inorganic Geochemistry Group

Title of project:

Tracing sources of selenium and iodine in precipitation from the high altitude sites Jungfraujoch and Pic du Midi

Part of this programme:

SNF PP00P2_163747

Project leader and team:

Dr. Julie Tolu, Prof. Dr. Lenny Winkel (project leaders)
Dr. Elke Suess

Project description:

Atmospheric deposition is a main source of essential nutrients and micronutrients (e.g., selenium and iodine) to terrestrial environments, including agricultural soils. Selenium (Se) is an essential element for humans. Low Se intakes, which can cause Se deficiency, have been estimated to affect up to 0.5–1 billion people worldwide [1]. The atmosphere is an important reservoir of Se (~13,000 to 19,000 tons of Se per year), supplying terrestrial environments and food crops with Se via wet deposition [2]. The element Iodine (I) plays a crucial role in biochemical processes in the body as it is the main component of thyroid hormones and of deiodinase enzymes, which are important for activation of these thyroid hormones [3]. Despite the fact, that the body requires relatively small amounts of I, deficiency disorders caused by inadequate intakes are widespread. Marine-derived precipitation has been suggested to be a main source of Se and I to terrestrial environments, including soils and crops [2, 4]. However, data are scarce and the origin of Se and I in continental rainfall is still largely unknown.

In the first part of this project (previous reporting period, main investigator Dr. Elke Suess) we studied rainfall compositions over time, including concentrations and elemental speciation of I and Se, as well as sulfur (S) and bromine (Br), which have similar chemical properties and environmental pathways as Se and I but occur in higher concentrations in rainfall. We analyzed precipitation from Jungfraujoch (JFJ), and another high-altitude station, i.e., Pic du Midi (Pyrenees, France, PDM), which receives more Atlantic air masses. At both sites, weekly precipitation samples were collected (JFJ 07/2015-09/2016, PDM 04/2015-10/2015 and 04/2016-09/2016) in an open sampler. Apart from analyzing precipitation chemistry, in the current reporting period we also carried out moisture source diagnostics in collaboration with Prof. Heini Wernli and his group at ETH Zurich. The results from these analyses have been linked to trace element content and DOC-$\delta^{13}C$ values (indicating sources of DOC in rainfall). Positive correlations between DOC $\delta^{13}C$-values, contributions of continental air and Se (at JFJ) and I (at PDM) indicate a potential biogenic continental origin of Se and I in summer at these locations. These results are in line with recent studies suggesting that terrestrial biogenic emissions constitute an important but largely unexplored atmospheric source of I and Se. A paper on this study is in progress.

Speciation analyses of Se, I, S and Br using HPLC-ICP-QQQ (Agilent 8800) revealed that these elements mainly occurred as inorganic and anionic species in the rainfall samples. However, in a number of weeks we found unidentified species of Se, I and S and Br, that we hypothesize to be of organic nature. Therefore, the next objective of the project was to identify these unknown species, which will help to better understand the sources and transport of these trace elements in the atmosphere (main investigator Dr. Julie Tolu). Furthermore, organic matter (OM) contains compounds that are highly specific for marine,

terrestrial vegetation, and different types of anthropogenic emissions (e.g., biomass burning, coal combustion), and could therefore provide further information on sources. A first step was aimed at characterizing the molecular composition of OM in combination with the quantification of Se, I, S and Br as well as other major and trace elements in both precipitation and aerosol samples. Precipitation samples were collected weekly over the entire year 2017 at JFJ and PDM, and aerosol samples were collected in summer 2015, 2016 and 2017 at Pic du Midi. Major and trace elements were quantified in the precipitation and the aerosols (after acid digestion) using ICP-QQQ (Agilent 8800). Then, for the aerosol samples, we used a recently optimized pyrolysis (Py)-GC/MS method which enables a high throughput characterization of OM molecular composition in solid samples containing low OM content, and provides specific proxies for OM sources and the degradation status of compounds [5]. In contrast, for precipitation samples, there is no existing, adequate method to characterize the OM molecular composition. This is specifically a challenge for determining OM in samples from high altitude stations where dissolved organic carbon (DOC) contents are extremely low <0.5 mg L^{-1}.

In order to analyse these low amounts of DOM, we first tried to develop a method combining i) solid phase extraction (SPE) to isolate and pre-concentrate dissolved OM from precipitation samples and ii) DOM characterization by Liquid Chromatography-Orbitrap-MS by adapting methods developed for seawater which contain similar DOM content than precipitations [6-7]. Different SPE procedures were tested, e.g., with and without acidification of the sample, different ratios between precipitation volume and mass of the SPE resin, and two liquid chromatographic separations were tested (reverse phase and HILIC). Despite optimization of DOM isolation/pre-concentration steps, only few tens of organic compound formulas could be determined with good reproducibility while in seawater, few thousands of organic compound formulas have been determined [7]. The low DOC content in precipitation samples at JFJ and PDM, together with limited amount of sample that can be collected over a week (max 1-2 L, versus >30L of seawater, was pre-concentrated) results in too low DOM concentrations in the isolates to characterize the overall OM molecular composition. In contrast, our approach combining elemental analyses with OM characterization by Py-GC/MS in aerosols appeared efficient to trace Se sources in the atmosphere as first data indicated. Indeed, our results shows that most of (trace) metals (e.g., Al, Co, Fe, Mn, Li, U), and in a lesser extent trace elements such as Se, Br, S and I, correlate with organic proxies for biomass burning and/or coal combustion. In addition, Se, S, I, and Br are strongly correlated to organic proxies for phytoplankton OM (chlorophylls and proteins) which reflects the volatilization of Se, S, I, Br from phytoplankton activity. Therefore, we are now focusing on the analysis of aerosols and stopped the collection of precipitation samples at JFJ in august 2017 for now. Once we will identify good OM proxies to trace sources and/or transport of Se, I, S and B in aerosols, it may possible to optimize/develop methods for analyzing those specific proxies in precipitation samples as well.

References:

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Key words:

Precipitation, aerosol, selenium, iodine, organic matter composition, HPLC, ICP-QQQ, Orbitrap-MS and Py-GC/MS

Internet data bases:

Data will be published in peer-reviewed journals. Unpublished data are available on request.

Collaborating partners/networks:

Dr. Jeroen Sonke, GET, Observatoire Midi-Pyrénées, Toulouse (France)
Prof. Heini Wernli, Dr. Franziska Aemisegger, Dr. Michael Sprenger, D-USYS, ETH Zürich

Scientific publications and public outreach 2017:

Conference papers

Suess, E, J.E. Sonke, L.H.E. Winkel, Selenium speciation in rainwater from high altitude locations, Oral presentation, Se2017, Stockholm, Sweden, August 13-17, 2017.

Suess, E, J.E. Sonke, L.H.E. Winkel, Sulfur, selenium and iodine speciation in rainwaters from high altitude locations, Oral Presentation, ICOBTE 2017, Zurich, Switzerland, July 16-20, 2017.

Invited talks on development of speciation methods for Se, I, Br, S (in German)

Suess, E., Speziierung mariner (Spuren)elemente (Se, I, Br, S) in Regenwässern, 19th ICP-QQQ user meeting, Agilent Technologies, Waldbronn, Germany, September 21-22, 2017.

Suess, E., Analyse von Se-, S-, Br-, und I-Spezies im Regenwasser mittels LC-ICP-QQQ, Metrohm IC user meeting, Metrohm AG, Zofingen, Switzerland, May 4, 2017.

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