Name of research institute or organization:

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

Title of project:

Iodine, selenium, bromine, and sulfur speciation in precipitation from Jungfraujoch and Pic du Midi

Part of this programme:

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Project leader and team:

Dr. Elke Suess, Prof. Dr. Lenny Winkel (project leaders)
Mrs. Caroline Stengel

Project description:

Atmospheric deposition is a main source of essential nutrients and micronutrients (e.g., iodine, selenium, and sulfur) to terrestrial environments (e.g., 1, 2 and publications therein), including agricultural soils. Due to changes in anthropogenic emissions over the last decade, especially in Europe and the United States, concentrations of sulfur, selenium and other elements in atmospheric deposition have declined and spatial deposition patterns have changed [3]. These changes may result in lower inputs of (micro)nutrients to soils and eventually in (micro)nutrient deficiency in soils and crops, which may affect human health. Furthermore, due to declining industrial emissions, natural sources may become relatively more important. For example biogenic emissions of sulfur and selenium, especially from the oceans may play an increasingly important role in determining elemental contents of these elements in rainfall. However, sources of iodine, selenium and sulfur in rainfall are still not well characterized.

Therefore, we investigated concentrations and elemental speciation of iodine (I), selenium (Se), sulfur (S) and other (trace) elements such as bromine (Br) in precipitation at Jungfraujoch (JFJ) and another high-altitude location in Europe, i.e., Pic du Midi (Pyrenees, France, PIC), which receives more marine air masses. At both sites, weekly precipitation samples were collected (JFJ 07/2015-09/2016, PIC 04/2015-10/2015 and 04/2016-09/2016) in an open sampler. Furthermore an Eigenbrodt wet-only sampler with precipitation sensor and temperature controlled sample room was used at PIC. We analyzed total concentrations and trace element speciation using (HPLC)-ICP-QQQ (Agilent 8800) with an analytical method initially developed for Se speciation only (using a Hypercarb column and a formic acid-methanol eluent) [4]. The use of oxygen as reaction gas in HPLC-ICP-QQQ analyses enabled the simultaneous detection of species of I, Se, S and Br. Furthermore, total concentrations of dissolved organic carbon (DOC) were measured (Shimadzu TOC-L CSH) as well as DOC-δ13C using isotope ratio mass spectrometry (GasBench II) [5].

In the precipitation samples from JFJ, total contents for I ranged from 0.04-1.46 ug per week and total Br concentrations ranged from 0.1 to 6.0 ug per week. Both elements did not show large seasonal variations. On the other hand, Se (< LOD-0.09 ug per week), S (8-1670 ug per week) and DOC (0.2-2.8 mg per week) had higher concentrations in spring and summer compared to winter and autumn. The speciation of I, Br, Se, and S was largely dominated by anionic inorganic species, namely iodate (IO_3^-, 64-98%) and iodide (I^-, 2-36%), bromide (Br^-, 82-98%), selenite ($HSeO_3^-$, 18-52%) and selenate (SeO_4^{2-}, 48-82%), and sulfate (SO_4^{2-}, 95-100%) (percentages as % of the species sum) throughout the year. Partial correlations (Fig. 1), controlled for precipitation, showed strong correlations between Br and I, in addition to weaker but significant correlations of Br and I with SO_4^{2-} and I with DOC. We did not find significant correlations between Methanesulfonic acid (MSA), an oxidation product of biogenic (marine) produced dimethylsulfide (DMS) [6], and any of the species of interest for

this study (e.g. Br^-) at JFJ. On the contrary, at PIC we found a significant correlation between MSA and Br^-, which hints to the importance of Br-compounds in the formation of MSA as also suggested by Frege et al. [7].

Further (statistical) analysis of the obtained data on total elemental concentrations, speciation and carbon isotopes is underway. It is expected that the results will be published in a peer-reviewed journal in 2017.

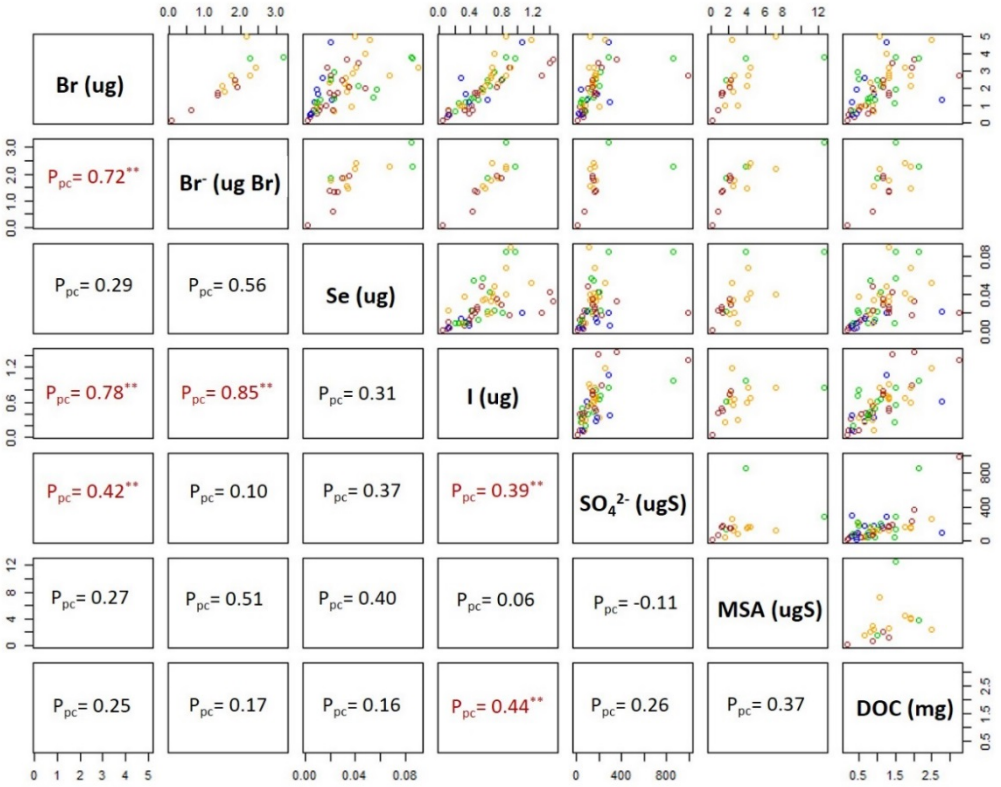

Figure 1. Partial correlations (p_{pc}) with controls on precipitation for total bromine (Br), bromide (Br^-), total selenium (Se), total iodine (I), sulfate (SO_4^{2-}), methanesulfonic acid (MSA), and dissolved organic carbon (DOC) in a precipitation time series at Jungfraujoch from July 2015 to September 2016. Scatter plots show seasonal data (green: spring, orange: summer, brown: autumn, and blue: winter). Significant correlations with $p < 0.01$ are marked **.

References:
(1) Fuge, R. and Johnson, C.C., Environ. Geochem. Health 1986, 8, 31 pp
(2) Winkel, L.H.E. et al., Environ. Sci.Tech. 2012, 46, 571 pp
(3) RoTAP, Contract Report to the Department for Environment, Food and Rural Affairs, Centre for Ecology & Hydrology, 2012
(4) Dauthieu et al., J. Chrom. A. 2006, 1114, 34 pp
(5) Lang, S. et al., Rapid Commun. Mass Spectrom. 2012, 26, 9 pp
(6) Gondwe, M. et al., Global Biogeochem. Cyc. 2003, 17(2), 1056 pp
(7) Frege, C. et al., Atmos. Chem. Phys. Discuss., 2016, doi: 10.5194/acp-2016-709

Key words:

Precipitation, rainfall, iodine, bromine, sulfur, selenium, speciation, HPLC, ICP-QQQ

Internet data bases:

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

Collaborating partners/networks:

Stefano Bernasconi, ETH Zurich, Switzerland
Stephan Henne, Empa, Dübendorf, Switzerland
Jeroen Sonke, CNRS, Toulouse, France

Scientific publications and public outreach 2016:

Conference abstracts

Suess, E., L.H.E. Winkel, Investigating Biogenic Sources and Speciation of Sulfur and Selenium in Rainfall, Goldschmidt Conference, Yokohama, Japan, June 26 - July 1, 2016, Gold2016:abs:4256, 2016.

Theses

Schlierenzauer, C., Analyses of Selenium in Rainwater Samples by Atomic Fluorescence Spectrometry, BSc Thesis, ETH Zurich, USYS, 2016.

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