

Ruprecht-Karls-Universität Heidelberg
Institut für Umwelt-Geochemie

**Observations of Iodine Speciation and Cycling in
the Hydrosphere**

Benjamin Silas Gilfedder

2008

Inaugural - Dissertation

Zur

Erlangung der Doktorwürde

der

Naturwissenschaftlich-Mathematischen Gesamtfakultät

der

Ruprecht – Karls – Universität

Heidelberg

vorgelegt von

BSc. (Hons) Benjamin Silas Gilfedder

Aus: Barkers vale, Australia

Tag der mündlichen Prüfung: 28. Februar 2008

Gutachter:

Prof. Dr. Harald Biester
Institut für Umwelt-Geochemie
Ruprechts-Karls-Universität Heidelberg
Im Neuenheimer Feld 236
D-69120 Heidelberg

Prof. Dr. Heinz Friedrich Schöler
Institut für Umwelt-Geochemie
Ruprechts-Karls-Universität Heidelberg
Im Neuenheimer Feld 236
D-69120 Heidelberg

Acknowledgements

It is difficult to know where to start with the acknowledgements since so many people have helped in various ways to make this project come together. I guess the logical place is to start at the top, with my supervisor, Professor Harald Biester. I would like to express my gratitude to Harald for allowing me to follow the unexpected paths that have developed during this work, despite the fact that some of these were a little off track from the original project aim. Harald also encouraged me to continue with method development and always believed that it would work in the end, despite the times when I was sure it was impossible to overcome the constant recovery of 42%! Luckily he was, of course, correct. Finally I would like to thank my Boss for beer on a number of occasions and dinner on at least one occasion down at the local 'Hofbräu'.

I would like to thank Professor Schöler for many useful and helpful discussions on chemistry in general and iodine chemistry in particular. These discussions helped to develop a deeper scientific understanding of iodine cycling in the environment. I would also like to thank Heinfried for introducing me to the 'Vodka Banana' and 'Pflaumenkuchen'. Next I would like to thank our group (current and past), Anne, Asher, Axel, and Frederik (Freddy) who helped with many many things (including iodine frogs) over the course of the last three years. I also need to thank Stefan Huber for interesting discussions and advice concerning mathematics. Our technicians also require a mention, Stefan and Silvia Rheinberger and Christian Scholz, for always being able to suggest a way to overcome technical problems, and providing much help. The Werkstatt guys also were very professional and also gave very important advice on the practical side of constructing instruments and sampling devices. I also thank the other people at our institute for the continued good vibe, the late Prof. German Müller, Prof. Bill Shotyk, Prof. Margot Isenbeck-Schröter, Dr. Basem Shomar, Dr. Andriy Cheburkin (especially for help with electronics), Dr. Michael Krachler, Torsten Hoffmann (especially for administrative help) and anyone else I have forgotten.

Next I would like to express my thanks and gratitude to Dr. Roland von Glasow for inspiring me to continue on the path of atmospheric science (and specifically the role of halogens) and particularly for the invitation to speak at the University of East Anglia, England, and the stimulating discussions this entailed. I also need to thank Roland and Matthias Poit for taking the snow samples from Summit Camp, Greenland, Joele Bauxmann and Katja Seitz for the rain samples from Mace Head, Ireland, and Fred McGregor for the rain sample from Oakura, New Zealand. I also express my thanks to Dr. Benjamin Murray for the invitation to Leeds to speak at their weekly colloquium and introducing me to Prof. John Plane and Prof. Dwayne Heard and their working groups.

Of course any acknowledgments would not be complete without mention of my trusty cooperation partners, Michael Petri at Lake Constance for many hours of argon and interesting discussions over good food and much excellent beer, Senchao Lai and Professor Thorsten Hoffmen from the University of Mainz for discussions about atmospheric iodine chemistry and the aerosol samples from Mace Head, and Dr. Martin Wessels for sediment samples from Lake Constance, the result of which remain unpublished.

Last but not least I would like to thank the support of my new family, Jessica and Ruben (bourn 29.10.07), for much tolerance and help during this project. Jessica deserves a special thanks for many hours of sampling at Lake Constance, the Alps and the Mummelsee, usually in all kinds of terrible weather (-15°C and snow to +15°C and rain to +30°C and sun). My father for continuing discussions on all aspects of science from the macroscale to the microscale and instilling my love of fireworks. My mother for a different perspective on life. Joy for many years of practical training. Boudica for the friendship.

Publication list and authors contribution

This thesis is based on five journal articles, three of which are published, one is published on-line in the discussions forum, and one submitted.

Chapter 1: Atmospheric section

Gilfedder, B. S., M. Petri, and H. Biester, Iodine speciation in rain and snow: Implications for the atmospheric iodine sink, *Journal of Geophysical Research*, 112, doi:10.1029/2006JD007356, 2007.

The sampling, laboratory work, and manuscript preparation was conducted by B.S. Gilfedder. M. Petri assisted with laboratory work and allowed the use of his laboratory and analytical infrastructure for all analysis. H. Biester supervised the work and planned the project.

Gilfedder, B. S., M. Petri, and H. Biester, Iodine and bromine speciation in snow and the effect of orographically induced precipitation, *Atmospheric Chemistry and Physics*, 7, 2661-2669, 2007.

B.S. Gilfedder conceived the idea, took the samples, conducted the laboratory work, and prepared the manuscript. M. Petri helped with laboratory work, allowed us to work in his laboratory, and provided valuable comments on the manuscript. H. Biester supervised the work and provided comments on the manuscript and funding for the project.

Gilfedder, B.S., Lai, S.C., Petri, M., Biester, H. and Hoffmann, T.: Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to droplet phases, *Atmospheric Chemistry and Physics*, Submitted, 2008.

Laboratory work, manuscript preparation and data interpretation was conducted by B.S. Gilfedder. Sampling of precipitation was done by various scientists, including B.S. Gilfedder, S.C. Lai and others listed in the acknowledgements. All aerosol samples were taken by S.C. Lai. M. Petri helped with laboratory work and provided comments on the manuscript. H. Biester and T. Hoffmann supervised the work and provided valuable comments on the manuscript.

Chapter 2: Terrestrial Environment

Gilfedder, B. S., F. Althoff, M. Petri, and H. Biester, A thermo extraction–UV/Vis spectrophotometric method for total iodine quantification in soils and sediments, *Analytical and Bioanalytical Chemistry, Online First*, DOI: 10.1007/s00216-007-1621-4, 2007.

B.S. Gilfedder wrote the manuscript and interpreted the data and did most of the laboratory work. F. Althoff helped with laboratory work and in setting up the analytical method. M. Petri helped with the statistical aspects in the work and provided much theoretical insights for the paper. H. Biester planned the project, supervised the work, and provided valuable information that helped with writing the paper.

Gilfedder, B. S., M. Petri, and H. Biester, Iodine speciation and cycling in limnic systems: observations from a humic rich headwater lake (Mummelsee), *Biogeosciences, Published on-line in BGD*, 2007.

Sampling, laboratory work, data interpretation, and manuscript preparation were conducted by B.S. Gilfedder. M. Petri helped with the analytical setup, analysis and provided valuable ideas for the paper. H. Biester supervised the work, planned the project, and helped with sampling on several occasions.

Confirmation of authors contribution

It is confirmed that B.S. Gilfedder's contribution to the papers presented in this thesis and listed in the 'publication list and authors contribution' is true, accurate, and justified.

Signature: Prof. Dr. Biester

Signature: F. Althoff.....

Declaration

This thesis contains no material which has been submitted or accepted for an award of any other degree or diploma in any university or institution.

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

Declared by: Benjamin Silas Gilfedder

Signature:.....

Dated on:

Erklärung

Hiermit erkläre ich, Benjamin Silas Gilfedder, geb. 23. März 1982, in Tomewin Australia, an Eides statt dass ich die vorgelegte Dissertation selbst verfasst und mich dabei keiner anderen als der von mir ausdrücklich bezeichneten Quellen und Hilfen bedient habe.

Ich Benjamin Silas Gilfedder, geb. 23. März 1982, in Tomewin Australia, erkläre zudem an Eides statt, dass ich an keiner anderen Stelle ein Prüfungsverfahren beantragt habe, dass ich die Dissertation nicht in dieser oder anderer Form bereits anderweitig als Prüfungsarbeit verwendet habe und dass ich sie an keiner anderen Fakultät als Dissertation vorgelegt habe.

Heidelberg, 19. Januar 2008

Summary

Iodine is an important element in oceanic, atmospheric, and terrestrial systems. Firstly, radical reactions in the troposphere can lead to significant ozone depletion, and secondly, nucleation of gaseous iodine molecules can produce new aerosol formation events, presenting possible direct and indirect natural cooling effects on climate. In the terrestrial environment iodine is a vital micronutrient for all mammals, with a lack of iodine intake leading to several debilitating disorders such as goiter and cretinism. The aim of this study was to investigate iodine systematics, and particularly speciation, in the atmosphere (aerosols, rain, and snow) and terrestrial hydrosphere (lakes) in order to gain a better understanding of how iodine moves between and within each environmental compartment. A subsidiary aim was to develop an inexpensive, but sensitive and accurate method for iodine quantification in soils and sediments using conventional analytical equipment. Rain and snow samples were taken from both northern (Germany, Switzerland, Ireland, Greenland) and southern (Australia, New Zealand, Chile) hemispheres whereas aerosols were obtained from Mace Head, Ireland using cascade (5 stages) and PM 2.5 impactors. Iodine cycling in lakes was investigated in the Mummelsee, a small headwater lake in the Black Forest. Speciation measurements were conducted by coupling an ion chromatograph to an ICP-MS and the organic fraction calculated as total iodine minus the inorganic species iodide and iodate.

Organically bound iodine was the most abundant fraction in the atmospheric aqueous phase, despite the fact that iodine oxides are currently thought to be the theoretical sink species. Aerosols from Mace Head, Ireland, contained a median of 50 pmol m^{-3} total iodine, with more than 90 % being associated with organic matter. Iodide was the next most abundant species (median 5 %) with iodate being the least abundant (median 0.8 %). Similar results were found in the precipitation samples from northern and southern hemispheres, with organic iodine composing over half of the total iodine, and in the snow from Greenland up to 88 %; although in general the organic fraction was lower in precipitation than in aerosols. Up to 5 unidentified peaks, representing iodine species in addition to iodide and iodate, were observed in aerosol and precipitation chromatograms, providing direct evidence for organic iodine compounds in aerosols and precipitation. While these species remain unidentified, they are thought to be anionic and relatively small (i.e. low molecular weight). It is suggested that these compounds and iodide form during (photolytic) decomposition of organo-I of high molecular weight, the organic material possibly stemming from the ocean surface microlayer. It was also found that orographically induced precipitation significantly effects iodine concentrations in snow, with iodine levels

decreasing exponentially with altitude over a transect in the Black Forest; indeed, more than halving (38 to 13 nmol l⁻¹) over an altitude change of 840 m and horizontal distance of only 5 km. It is suggested that orographic effects may be more important than lateral distance from the ocean in determining iodine levels in continental precipitation.

Once precipitation enters terrestrial ecosystems it may interact with soils, rocks, and biota. Iodine levels in the Mummelsee were very similar to rain and snow, averaging 15.2 ± 2.4 nmol l⁻¹, suggesting at very little iodine input from the catchment geology. Iodine in the lake and the spring inflow was dominantly associated with organic matter with, on average, 85 ± 7 % organically bound. However, inorganic iodine cycling in the lake was also important, and displayed pronounced redox chemistry, with both iodide release from the sediments and iodate reduction in the hypolimnion during anoxic stratified conditions. The iodide flux (up to 10.1 nmol m⁻² d⁻¹) back into the water column is probably due to the decomposition of detritus in the top few centimeters of the sediments. In contrast to the hypolimnion, iodide was removed from the epilimnion during the summer and autumn months, whereas iodate levels increased slightly over the same time period, suggesting at the importance of biological reactions. This was supported by a sediment core that contained high iodine concentrations, averaging 92 μmol kg⁻¹ total iodine, and a significant correlation with organic carbon ($p < 0.001$).

The analytical method entailed combusting sediment or soil samples in the oven of an AOX apparatus at 1000 °C and trapping the vapours in Milli-Q water. The solution was then analysed for iodine by a kinetic UV/Vis photospectrometry whereby iodide quantitatively catalyses the oxidation of As³⁺ and reduction of chromophoric Ce⁴⁺. The method was shown to be sensitive (detection limit 49 ng at 95 % confidence) and precise with relative standard deviations less than 5%.

In conclusion, while this work has shown that organic matter plays a very important role in the hydrosphere, particularly in regards to iodine cycling, considerably more work needs to be conducted on themes such as identifying the organic iodine species, how is the iodine bound to the organic material and what is the role of organisms in the formation of organic iodine. With the current interest in iodine chemistry it is hoped that these and many other pressing questions will be answered in the near future.

Zusammenfassung

Jod ist ein wichtiges chemisches Element des ozeanischen, atmosphärischen und terrestrischen Ökosystems. So führen seine Radikalreaktionen in der Troposphäre zu bedeutendem Ozonabbau, aber auch kann die Nukleation gasförmiger Jodverbindungen zur Produktion neuer Aerosole führen, welche direkte und indirekte kühlende Effekte auf das Klima haben können. In der terrestrischen Umwelt ist Jod ein essentielles Spurenelement für alle Säuger und ein Joddefizit in der Ernährung führt zu verschiedenen Behinderungen wie z.B. Kropfbildung oder Kretinismus. Ziel dieser Studie war, das Verhalten des Elementes Jod in der Umwelt zu untersuchen und dabei vor allem seine Speziation in der Atmosphäre (Aerosole, Regen und Schnee) sowie der terrestrischen Hydrosphäre (Seen), um letztlich ein tieferes Verständnis für den Jodkreislauf zu gewinnen. Ein ergänzendes Ziel war die Entwicklung einer preiswerten, aber dennoch empfindlichen und präzisen Methode für den quantitativen Nachweis von Jod in Böden und Sedimenten mittels konventioneller Laborausstattung. Regen- und Schneeproben wurden sowohl in der Nordhalbkugel (Deutschland, Schweiz, Irland, Griechenland) als auch der Südhalbkugel (Australien, Neuseeland, Patagonien) genommen. Aerosole wurden mittels Kaskaden- (5 Stufen) und PM 2.5-Impaktor in Mace Head, Irland, gesammelt. Der limnische Jodkreislauf wurde am Beispiel des Mummelsees, einem kleinen oberläufigen Gewässer im Schwarzwald, untersucht. Untersuchungen der Speziation wurden durch Verknüpfung eines Ionenchromatographens mit einem ICP-MS durchgeführt und die organische Fraktion als Gesamtjod minus anorganischer Anteil (Jodid und Jodat) berechnet.

Die Untersuchungen zeigten, dass organisches Jod den größten Anteil atmosphärischer wässriger Phasen ausmacht, obwohl das momentane Verständnis Jodoxid als theoretische Senkenspezies annimmt. Aerosole von Mace Head, Irland, bestanden im Mittel aus 50 pmol m^{-3} Gesamtjod, von dem über 90% mit organischem Material assoziiert war. Jodid war die zweithäufigste Spezies (im Mittel 5%) und Jodat am geringsten vertreten (im Mittel 0.8%). Ähnliche Ergebnisse wurden für die Niederschlagsproben der Nord- und Südhalbkugel gefunden, in denen die organische Fraktion mehr als die Hälfte des Gesamtjods ausmachte und in Schneeproben aus Grönland sogar bis 88% erreichte. Insgesamt waren sowohl organische Fraktion als auch Gesamtkonzentration im Niederschlag stets geringer als in Aerosolen. In den Chromatogrammen der Aerosole und des Niederschlags wurden zusätzlich zu Jodid und Jodat 5 weitere Peaks beobachtet, die das Vorkommen von organischen Jodverbindungen in Aerosolen und Niederschlag bestätigen. Es wird angenommen, dass diese Spezies von Aerosolen zum Niederschlag überführt werden. Obwohl diese Verbindungen selbst unbekannt sind, wird vermutet,

dass es sich um anionische Spezies geringer molekularer Größe handelt. Es wird hier vorgeschlagen, dass die unbekanntes Verbindungen und Jodid während des (photolytischen) Abbaus organischer Jodverbindungen höheren molekularen Gewichts entstehen, die ihrerseits wahrscheinlich der ozeanischen Oberflächenschicht entstammen. Außerdem wurde festgestellt, dass orographisch induzierter Niederschlag Jodkonzentrationen im Schnee signifikant beeinflusst, mit exponentiell abnehmenden Jodgehalten bei ansteigender Höhe eines Transektes im Schwarzwald. Tatsächlich fiel die Konzentration über die Hälfte, von 38 zu 13 nmol l⁻¹ über einem Höhenunterschied von 840m und einer horizontalen Distanz von nur 5 km ab. Möglicherweise ist der Einfluss orographischer Effekte an der Jodkonzentration in kontinentalem Niederschlag größer als die laterale Distanz vom Ozean.

Sobald der Niederschlag in die terrestrischen Ökosysteme eintritt, beginnen Wechselwirkungen mit Boden, Gestein und den dort lebenden Organismen. Die Jodgehalte im Mummelsee betragen im Durchschnitt 15.2 ± 2.4 nmol l⁻¹ und waren somit denen im Regen und Schnee sehr ähnlich. Daraus ist zu schließen, dass die Geologie des Einzugsgebietes nur einen sehr geringen Einfluss hat. Jod im See und aus dem Quellzufluss war hauptsächlich mit organischem Material assoziiert, im Durchschnitt zu 85 ± 7 %. Dennoch spielen anorganische Jodkreisläufe eine wichtige Rolle im limnischen System, in dem ausgeprägte Redoxprozesse erkennbar sind. So wird bei anoxischer Stratifikation des Sees Jodid aus dem Sediment freigesetzt und Jodat im Hypolimnion reduziert. Der Jodidfluss (bis zu 10.1 nmol m⁻² d⁻¹) in die Wassersäule entstammt wahrscheinlich sowohl dem organischen Abbau in den obersten Zentimetern des Sedimentes als auch der Mobilität dieser Spezies unter reduzierten Bedingungen. Im Gegensatz zum Hypolimnion wurde Jodid im Epilimnion während der Sommer- und Herbstmonate entfernt, wobei die Jodatgehalte über dem gleichen Zeitraum leicht anstiegen. Dies deutet auf den wichtigen Einfluss biologischer Reaktionen hin. Darauf wiesen auch hohe Jodkonzentrationen in einem Sedimentbohrkern (durchschnittlich 92 µmol kg⁻¹) und die signifikante Korrelation ($p < 0.001$) mit organischem Kohlenstoff hin.

Die entwickelte, analytische Methode beinhaltet Verbrennung der Sediment- oder Bodenprobe im Ofen eines AOX Gerätes bei 1000°C und das Auffangen der Dämpfe in Milli-Q Wasser. Diese Lösung wird mittels UV/Vis Photospektrometrie auf Jod analysiert, wobei Jodid quantitativ die Oxidation von As³⁺ und die Reduktion des chromatophoren Ce⁴⁺ katalysiert. Es wurde aufgezeigt, dass diese Methode mit relativer Standardabweichung von unter 5% präzise und sensitiv (Nachweisgrenze 49 ng bei einem Konfidenzintervall von 95 %) ist.

Zusammenfassend kann gesagt werden, dass diese Arbeit den wichtigen Einfluss organischen Materials in der Hydrosphäre, insbesondere im Zusammenhang mit dem Jodkreislauf, gezeigt hat. Deutlich mehr Forschung muss in diesem Bereich erfolgen, um z.B. zu klären, um welche unbekannt organischen Jodverbindungen es sich handelt, oder wie Jod sich mit organischem Material verbindet und welche Rolle biologische Prozesse bei der Bildung haben. Auf Grund des derzeitigen wissenschaftlichen Interesses an der Jodchemie besteht die Hoffnung, dass diese und weitere Fragen in baldiger Zukunft geklärt werden.

Table of Contents

Chapter 1: Introduction	
1.0 Introduction	2
1.1 Current state of knowlwdge	2
1.1.1 Biogeochemical cycles	2
1.1.2 Discovery of iodine and brief history	3
1.1.3 Oceans	4
1.1.4 Atmosphere	6
1.1.4.1 Gas phase	6
1.1.4.2 New particle formation	10
1.1.4.3 Precipitation	13
1.1.5 Terrestrial environment	15
1.2 Aims of this work	20
1.2.1 Methods	22
1.3 Summery of Findings	24
1.3.1 Iodine speciation in rain and snow: Implications for the atmospheric iodine sink	24
1.3.2 Iodine and Bromine speciation in snow and the effect of orographically induced precipitation	25
1.3.3 Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to droplet phases	26
1.3.4 A thermo extraction–UV/Vis spectrophotometric method for total iodine quantification in soils and sediments	28
1.3.5 Iodine speciation and cycling in limnic systems: observations from a humic headwater lake (Mummelsee)	28
1.4 Conclusions	31
1.5 References	33
Chapter 2:	41
Atmosphere	41
2.1 Iodine speciation in rain and snow: Implications for the atmospheric iodine sink	42
Abstract:	42
2.1.1 Introduction	42
2.1.2 Methods:	43
2.1.3 Results	44
2.1.3.1 Total iodine concentrations and its terrestrial distribution	44
2.1.3.2 Iodine speciation and the atmospheric iodine sink	47
2.1.4 Conclusions	50
Acknowledgements	50
2.1.5 References	51
Supplementary material	53
2.2 Iodine and Bromine speciation in snow and the effect of orographically induced precipitation	56
Abstract	56
2.2.1 Introduction	56
2.2.2 Methods	58
2.2.3 Results	60
2.2.4 Discussion	64
2.2.4.1 Microphysical processes	64
2.2.4.2 Speciation	66
2.2.4.3 Origin of the iodine and bromine	67
2.2.5 Conclusion	67
Acknowledgments	68
2.2.6 References	68
Supplementary material	70
2.3 Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to droplet phases	76

Abstract	76
2.3.1 Introduction	76
2.3.2 Methods:	78
2.3.2.1 Aerosol sampling	78
2.3.2.2 Precipitation sampling	79
2.3.2.3 Analytics	79
2.3.3 Results	80
2.3.3.1 Iodine speciation in aerosols and rain from Mace Head	80
2.3.3.2 Iodine speciation in rain and snow samples	87
2.3.4 Discussion	90
2.3.5 Conclusions	94
Acknowledgements	94
Supplementary material	95
References	102
Chapter 3:	105
Terrestrial systems	105
3.1 A thermo extraction-UV/Vis-photospectrometric method for total iodine quantification in soils and sediments	106
Abstract	106
3.1.1 Introduction	106
3.1.2 Material and methods	107
3.1.2.1 Chemicals	107
3.1.2.2 Thermal iodine extraction	108
3.1.2.3 Quantification	109
3.1.2.4 Samples	111
3.1.2.5 Detection limit	112
3.1.3 Results and Discussion	112
3.1.3.1 Reference materials	112
3.1.3.2 Real samples	114
3.1.4 Conclusions	115
3.1.5 Acknowledgements	116
References	116
3.2 Iodine speciation and cycling in limnic systems: observations from a humic rich headwater lake (Mummelsee)	118
Abstract	118
3.2.1 Introduction	118
3.2.2 Study site and Methods	120
3.2.2.1 Water samples	121
3.2.2.2 Sediment core	123
3.2.3 Results	124
3.2.3.1 Temperature profiles and stratification	124
3.2.3.2 Iodine speciation: Spring-Summer-Autumn	125
3.2.3.3 Iodine speciation: winter and spring-2006	129
3.2.3.4 Inflow	129
3.2.3.5 Sediment core	130
3.2.4 Discussion	132
3.2.4.1 Iodide	133
3.2.4.2 Iodate	136
3.2.4.3 Organically bound iodine	138
3.2.4.4 Sediment core	140
3.2.5 Conclusions	140
Acknowledgements	141
3.2.6 References	141
Supplementary information	144

Chapter 1:

Introduction

1.0 Introduction

1.1 Current state of knowledge

1.1.1 Biogeochemical cycles

Element cycling through and between our environmental compartments is a unifying theme in the geosciences (*geosciences* used here in its broadest sense). Vital elements for life such as C, N, P, metals such as Ca and K and the halogens F, Cl, Br, and I are continually moving between the geosphere (largely pertaining to rocks), pedosphere, biosphere, hydrosphere, and atmosphere. The cycling of elements has been of interest since the early days of science, however the actual interaction and interdependence between the spheres on a quantitative level has only recently received a concentrated effort in all areas of sciences. Such a quantitative understanding is vital in learning how the different natural compartments shape and influence our world, and indeed how we as part of this system, play a role in global dynamics.

Life as a driving force on global dynamics and element cycles was brought to the forefront of both scientific and public attention initially by Lovelock, (1979) with the *Gaia theory* and subsequently backed up with a strong scientific basis by Charlson et al. (1987) with what was to be known as *the CLAW hypothesis* (after the authors names: Charlson, Lovelock, Andreae, and Warren). Charlson et al. (1987) demonstrated in a quantitative manner that emissions of dimethyl sulfide (DMS) produced by marine phytoplankton and subsequent formation of cloud condensation nuclei (CCN), and thus droplet number density and cloud cover, could significantly influence the earth's albedo and so also global climate. In this scheme oxidation and nucleation of DMS and further production of clouds was related to changes in phytoplankton community structure, which in turn was a function of sea temperature and solar radiation. As such, organisms (unknowingly) could regulate the earth's climate to suit the sustainable progression of life. What is interesting in the CLAW model is that through a series of negative feedback mechanisms the temperature of the atmosphere is able to stay relatively stable despite changes in external forcing, such as increasing solar luminosity. Despite the controversy this created within the geosciences, interactions and cycling between the biosphere and the other spheres (particularly the atmosphere) to sustain life has received increasing attention, albeit under more conservative names than 'Gaia' as proposed by Lovelock, (1972). Moreover, many elements other than sulfur have been seen to move from one sphere to another. The elucidation of such pathways has allowed a better understanding of the environment in which we dwell, and the natural processes on which we, as a species, depend.

One of the most interesting points in the cycling of the elements is that they appear in many respects to operate on a fractal basis. Within each of the spheres, there exists a multitude of cycles at different scales, both biological and abiological. For example, carbon cycling works on scales from microbiological communities in the soils, which break down large macromolecules to be used as an energy source for higher organisms, to photosynthesis which produces the annual oscillations in atmospheric carbon dioxide concentrations observed in the Keeling curve from Mauna Loa (the most recent data can be found at <http://scrippsco2.ucsd.edu/>) The interconnectedness of these systems is complex, and as mentioned above for sulfur in the DMS cycle, involves feedbacks that often mean that the cycles cannot be modeled as a combination of simple linear dynamics.

One such element that has only recently received considerable attention is iodine, a biophilic element that is also a required nutrient for all mammals (despite its sparse abundance in the terrestrial environment) (de Benoist et al., 2004). Iodine is transferred between the spheres on different time scales and in different chemical forms (species). However, the dominant transfer pathway is either through the atmosphere as reactive gases (e.g. I_2 , CH_2I_2 , CH_2ICl , CH_3I) or in the aqueous phase (i.e. aerosols, rain, rivers, lakes and oceans). The largest iodine reservoirs are soils, rocks and the ocean (Fuge and Johnson, 1986). As in most systems these phases are not mutually exclusive, with photolysis of gaseous iodine compounds leading to uptake on, or even formation of, aerosols, which can be transferred to rain, soils, rivers, and lakes. Factors governing the migration through, and reactivity within, each subsystem are largely determined by the components in that system and also by the iodine species present. An interesting contrasting example is firstly iodide (I^-), which has very little affinity for sorption sites on soil and so can migrate readily to rivers and streams, and secondly iodate (IO_3^-) which is strongly sorbed to clay and Fe oxide surfaces (Neal and Truesdale, 1976; Ullman and Aller, 1980).

1.1.2 Discovery of iodine and brief history

It is interesting to note that iodine was first discovered in 1811 (by Bernard Courtois) by accidental addition of excess sulfuric acid to a vat containing seaweed residues from the French Coast. This subsequently led to rapid volatilization of I_2 gas which then condensed on cold surfaces as I_2 crystals. Such information may seem trivial at first, but as will be seen the role played by coastal seaweed, in terms of its high iodine content and emissions of iodine compounds, such as I_2 , is of vital importance in many parts of the iodine cycle.

Iodine in aerosols and precipitation became of interest in the atmospheric sciences, despite some earlier work, by studies conducted at Mauna Loa, Hawaii, by Duce et al., (1963; 1965; 1967) and

Duce and Woodcock, (1971). These authors found, in contrast to the other halogens, that iodine was strongly enriched relative to its oceanic source. Indeed, enrichment factors relative to Cl in aerosols and precipitation were on the order of 1000 times. This was some of the first evidence that iodine was a biogenic element that was efficiently transferred from the ocean into the atmosphere, in stark contrast to the other halogens. At a similar time, iodine speciation in the ocean was gaining attention, particularly with the observation that iodide and iodate were not in thermodynamic equilibrium in the surface ocean, with iodide levels a few orders of magnitude higher than predicted (Sugawara and Terada, 1967; Luther et al., 1995). This was attributed to biological reduction of iodate and excretion of iodide in the surface waters, the most convincing field evidence coming from Elderfield and Truesdale, (1980). Some of the first evidence for iodine emissions from the ocean came from laboratory studies by Miyake and Tsunogai, (1963) and field samples over the open ocean by Lovelock et al., (1973), further suggesting important biological and photolytic components in the iodine cycle. Iodine quantification in the terrestrial aquatic environment, particularly in regards to speciation, only gained interest in the 1980s (Jones and Truesdale, 1984). This may have been due to the low levels of iodine in freshwaters, although Duce et al., (1963) had developed a sensitive neutron activation technique that was capable of quantifying total iodine into the $\mu\text{g l}^{-1}$ range. Moreover, iodine cycling in rivers and lakes was largely thought to be the same as that in the ocean, with biology playing a role in maintaining the disequilibrium between iodide and iodate whereas organic iodine species were believed to be negligible.

Since these early studies significant research has been conducted in all of these spheres on iodine cycling within and between environmental compartments. The following section will review the most pertinent developments in each of the areas of interest to this thesis: **The Ocean**, as a source of atmospheric iodine. **The Atmosphere**, as one of the most important mediums for iodine cycling in terms of iodine species transformations, climate influences, and transport of iodine from the ocean to the terrestrial ecosystems. Finally, I will confine the **Terrestrial Environment** in this work primarily to the terrestrial aqueous environment i.e. iodine in rivers and lakes but will also give a limited review of iodine in soils and sediments as such processes will undoubtedly impact on aqueous geochemistry.

1.1.3 Oceans

Iodine concentrations in the oceans tend to vary slightly with salinity; however, when normalized to 35 ‰ it is relatively homogeneous at $58 \mu\text{g l}^{-1}$ ($0.46 \mu\text{mol l}^{-1}$) (Elderfield and Truesdale, 1980). Theoretically, based on conventional thermodynamics, iodate should be the only detectable species in the ocean with IO_3^-/I^- ratios on the order of $10^{13.5}$ (Luther et al., 1995). The continual

observation of iodide in surface waters, which correlates very well with a decrease in iodate levels, is thought to be due to biological reduction of iodate (Sugawara and Terada, 1967; Elderfield and Truesdale, 1980; Jickells et al., 1988; Tian and Nicolas, 1995; Chance et al., 2007). This may occur through coupling to nitrate uptake (nitrate reductase), as suggested by early work; however the actual mechanism has been very difficult to elucidate with evidence both for, and against, nitrate related reduction (Sugawara and Terada, 1967; Butler et al., 1981; Tian and Nicolas, 1995; Wong et al., 2002; Truesdale et al., 2003; Chance et al., 2007). It has also been shown that decomposition of organically bound iodine in near-shore waters produces iodide, although concentrations of organic iodine species in the open ocean water are thought to be relatively low (Wong and Cheng, 1998). In addition to dissolved iodine, particulate iodine plays an important role in removing iodine from the surface ocean to the sediments and deep water (Wong et al., 1976).

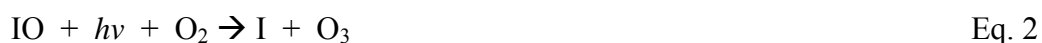
Since the oceans cover the largest surface area on earth, they are potentially the most important contributor to atmospheric iodine budgets. In most cases emission of volatile iodine species such as I_2 , CH_3I , C_3H_7I , CH_2I_2 , CH_2ICl and CH_2IBr have been related to biological production. There is also some strong evidence for abiological production of CH_3I , related to photolytic processes or Fe-catalyzed cycles (Richter and Wallace, 2004; Williams et al., 2007). It has been postulated that biological production of volatile organic iodine compounds is a defense mechanism against environmental stress such as ozone or bacterial attack (Palmer et al., 2005), and is thought to be enzymatic (Küpper et al., 1998). Unfortunately, the literature is strongly biased towards CH_3I concentrations and fluxes over the oceans despite the fact that less stable iodine compounds (e.g. CH_2I_2) would have the same impact on atmospheric processes at one thousandth the concentration (Carpenter, 2003). This is due to the relatively long lifetime of CH_3I (about 5 days) against photolytic decomposition compared to more reactive volatile halogen species (von Glasow and Crutzen, 2007). The emission flux of each species into the atmosphere is a product of the source strength multiplied by the surface area, and therefore despite the very low area of the coastal zone their very large fluxes may be sufficient to match open ocean fluxes of reactive iodine species such as I_2 and CH_2I_2 . It is also important to note that the less stable volatile iodine compounds also decompose in the water column, so that despite their biological production they may have only a limited effect on atmospheric processes (Martino et al., 2006; Jones and Carpenter, 2007). Some of these compounds also undergo transformations (such as electrophilic substitution) in seawater into more stable volatile compounds, which can then degas to the atmosphere. A prime example is CH_2I_2 , which reacts with Cl^- to form CH_2ICl ; a product that has been observed in the remote marine boundary layer (Carpenter et al., 2003; Jones and Carpenter, 2007).

1.1.4 Atmosphere

1.1.4.1 Gas phase

Iodine is emitted into the marine boundary layer as simple short chain organohalogens, the most important being CH_3I , $\text{C}_3\text{H}_7\text{I}$, CH_2I_2 , CH_2ICl and CH_2IBr . Recently, I_2 has also been observed in coastal environments, emitted from macroalgae such as *Laminaria sp.* during oxidative stress (Palmer et al., 2005), and is thought to be the largest contributor of iodine radicals in these areas (McFiggans et al., 2004; Saiz-Lopez and Plane, 2004; McFiggans, 2005; O'Dowd and Hoffmann, 2005; Peters et al., 2005). It remains to be seen how widespread I_2 emissions are, however due to its rapid photolysis and high iodine radical yield per mole I_2 photolysed, it has the potential to have a major influence in the marine boundary layer. It must also be noted that, in contrast to Br and Cl, aerosols derived from the ocean surface are a net sink for iodine rather than a source, with iodine enrichment factors in aerosols and precipitation around 1000 times and in extreme cases up to 16000 times sea water (Duce and Woodcock, 1971; Moyers and Duce, 1972; Sturges and Barrie, 1988).

Once iodine is emitted into the atmosphere it undergoes a complex series of radical reactions, summarized concisely in a review paper by von Glasow and Crutzen, (2007) (Figure 1). The most important parts of the atmospheric iodine cycle are, 1) the ability to destroy ozone in much the same manner as Cl and Br, and 2) nucleation of iodine gases to form new nanometer sized aerosols. The classic ozone destroying reaction can be written as:



This is a null cycle with no net change. However, IO is also able to react with other compounds in the atmosphere to catalytically destroy ozone, for example:



X is Cl, Br or I and subscript aq denotes the reaction is taking place in the liquid phase (aerosols or precipitation). Iodine radicals can also be formed by the IO-IO self reaction:



Which is also equivalent to:



The halogen radical released can cycle back into Eq. 1 to destroy more ozone, whereas OIO may be the monomer unit for aerosol condensation since it is relatively stable against photolysis (Hoffmann et al., 2001; von Glasow and Crutzen, 2007). Reactions with nitrogen dioxide occur by:



Again releasing iodine radicals to react via Eq.1. The terminal reaction for iodine is thought to be oxidation to higher iodine oxides such as I_2O_5 (Saunders and Plane, 2005) and uptake by aerosols and droplets, although these oxides remain to be found in field samples (Baker, 2005; Gilfedder et al., 2007a,b). Evidence for an important role of iodine in ozone destruction came from the direct observation of IO in the boundary layer in the late 1990s (Alicke et al., 1999), and has since been identified in many coastal environments using LP-DOAS (long path differential optical absorption spectrometry), for example, Mace Head Ireland, Dagebüll Germany, Lilia and Roscoff, France, (Saiz-Lopez and Plane, 2004; Peters et al., 2005; Whalley et al., 2007). Observations from non-coastal environments are less numerous, but include the Arctic (Wittrock et al., 2000), Antarctica (Saiz-Lopez et al., 2007b), the Dead Sea (Zingler and Platt, 2005), Cape Grim, Tasmania (as an open ocean signal), Tenerife, (Allan et al., 2000) and the stratosphere (Bösch et al., 2003). A summary of IO measurements by DOAS is presented in Peters et al., (2005). One of the drawbacks of DOAS measurements is that it does not capture iodine emissions on small scales, for example inter tidal zones, averaging IO levels over a light path of at least a few km. Interestingly two novel methods have recently been employed for point IO measurements, LIF (laser induced fluorescence) and CRDS (cavity ring-down spectroscopy), both of which appear to support a primarily coastal source of iodine emissions (Wada et al., 2007; Whalley et al., 2007).

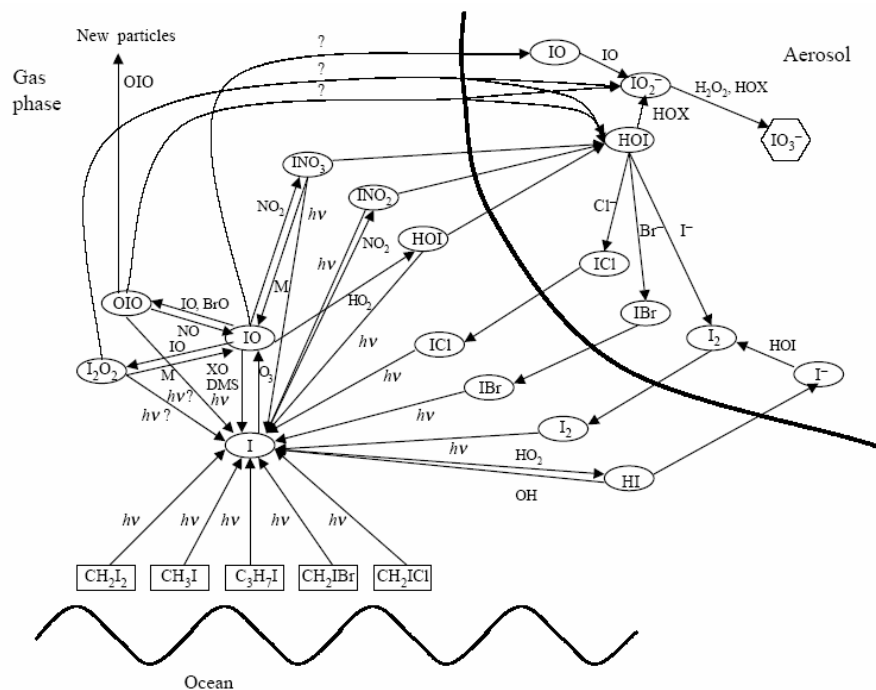


Figure 1: Schematic of iodine reactions in the marine boundary layer (von Glasow and Crutzen, 2003).

Some interesting and potentially important chemical feedbacks can occur through these reactions. Perhaps most significantly decreasing the HO_2/OH ratio, and thus affecting oxidation capacity of the atmosphere (Bloss et al., 2005). Such effects have been noted at Mace Head, Ireland (Bloss et al., 2005) and most recently in Antarctica (Saiz-Lopez et al., 2007b). It is important to note here that iodine's ability to destroy ozone is largely confined to the troposphere due to its reactivity. We note however that iodine may be transported into the stratosphere (Wittrock et al., 2000), perhaps associated with tropospheric aerosols, and thus may play a limited role there as well (see Figure 3 in Murphy et al., 2007).

While ozone depletion by the halogens, and iodine in particular, are important for the marine boundary layer, iodine's effects can be most significant, and most noticeable, in the Polar Regions during spring. Indeed, complete ozone depletion events (ODE) have been observed in the arctic under exceptionally stable boundary layer conditions, and are thought to be a result of halogen chemistry (Tarasick and Bottenheim, 2002; Hönninger et al., 2004). The rapid increase in tropospheric bromine during polar spring has been termed the '*bromine explosion*' (Frieß et al., 2004) and a similar explosion has also been observed for iodine. The first observations of IO in the Antarctic were made by Frieß et al., (2001). These authors found that the IO was most likely confined to the boundary layer and observed concentrations up to 10 pptv during the summer of 1999. More recently, Saiz-Lopez et al., (2007b) have produced LP-DOAS IO data from Halley station, Antarctica, that show IO levels up to 20 pptv; some of the highest values to date. They also

observed a strong seasonal cycle, with highest levels of IO occurring in spring, consistent with the iodine explosion hypothesis mentioned above (Figure 2). Interestingly, they also note a second smaller peak in IO levels during the autumn, which is not observed for bromine, suggesting that IO precursors have a different origin than BrO. Such observations are also consistent with satellite data retrieved from the SCIAMACHY satellite (Saiz-Lopez et al., 2007a; Schönhardt et al., 2007), and is thought to result from biological iodine emissions from the underside of the sea ice (Figure 3).

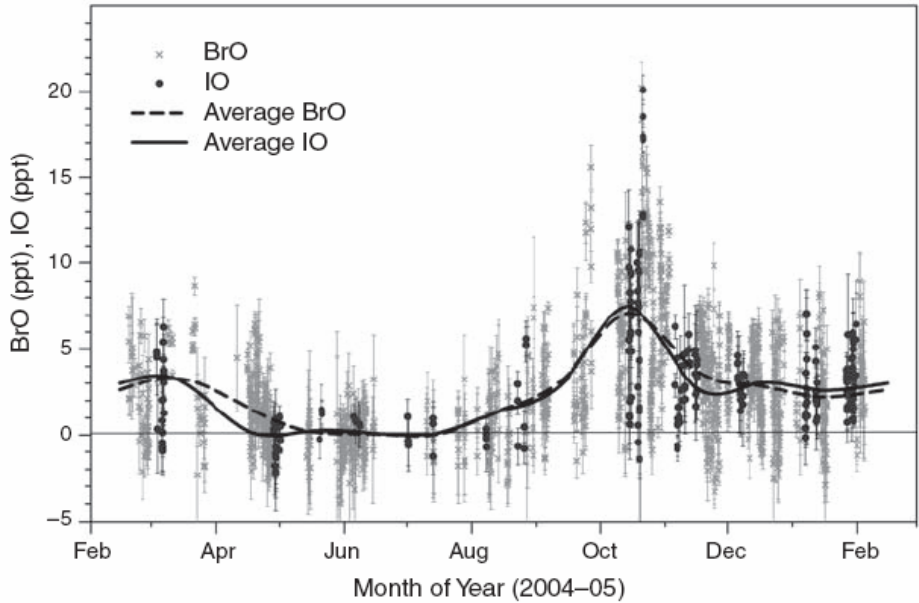


Figure 2: IO and BrO levels from Halley station, Antarctica (Saiz-Lopez et al., 2007b).

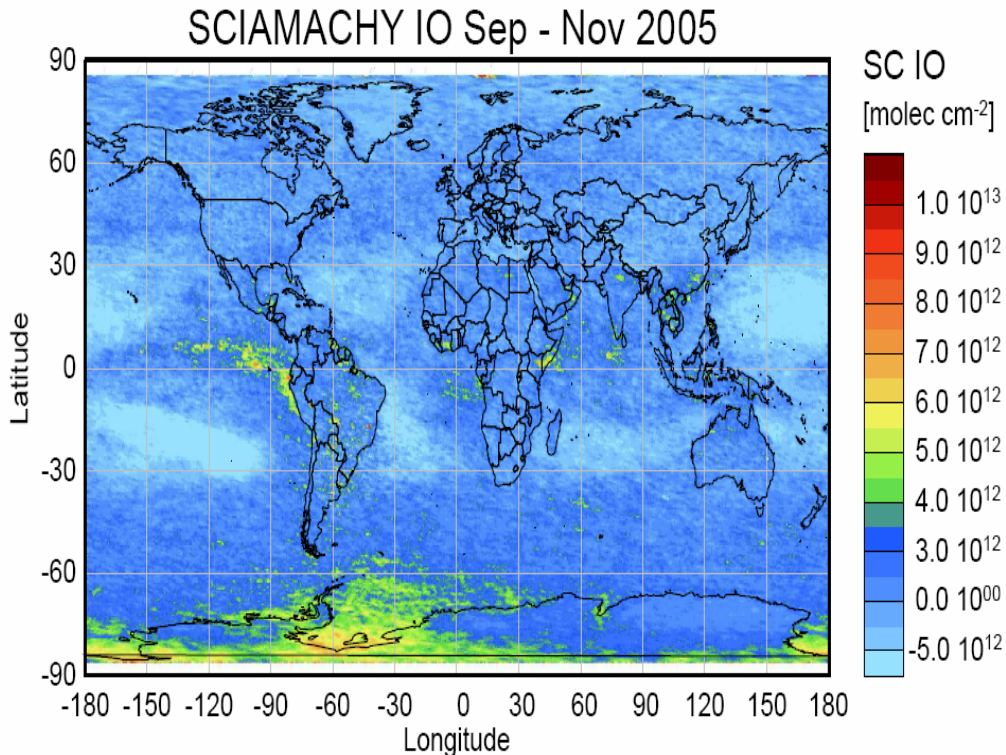


Figure 3: Global iodine oxide levels as observed from space (Schönhardt et al., 2007)

1.1.4.2 New particle formation

One of the most novel and interesting aspects of atmospheric iodine chemistry is nucleation of gaseous iodine precursors (most importantly I_2 and CH_2I_2) to form new aerosol particles. If the global flux of these particles is large enough they could have a significant cooling influence on climate (by increasing albedo) (1) directly through scattering a reflectance of incoming solar radiation back out to space (degree of reflectivity verses absorption depending on optical properties such as colour and shape), and (2) indirectly through increasing the number of cloud condensation nuclei, hence droplet number concentrations and further scattering and reflectance of solar radiation (Caine, 2007). Indeed, one of the least understood parts of current global energy budgets is the radiative forcing introduced by aerosols. For example, Ramanathan et al., (2001) have found that the top of atmosphere forcing by aerosols alone could rival (but as a negative force) that of greenhouse gases. This climatic effect is similar to the suggested DMS-aerosol-cloud feedback system introduced in the first section of this thesis.

Iodine nucleation was first discovered in chamber experiments using CH_3I by Cox and Coker, (1983), but was in essence ‘rediscovered’ by Hoffmann et al., (2001) in an attempt to explain the nucleation bursts (up to 10^6 particles per cm^{-3}) observed at Mace Head, Ireland (Figure 4). These authors exposed CH_2I_2 to ozone and light within an atmospheric simulation chamber and found very large particle production. These experiments were conducted more comprehensively (i.e. within the Caltex smog chamber, and product analysis by AMS-Aerosol Mass Spectrometry) by O’Dowd et al., (2002), who proposed that iodine emissions and aerosol formation could be radiatively important if nucleation also occurred over the open ocean.

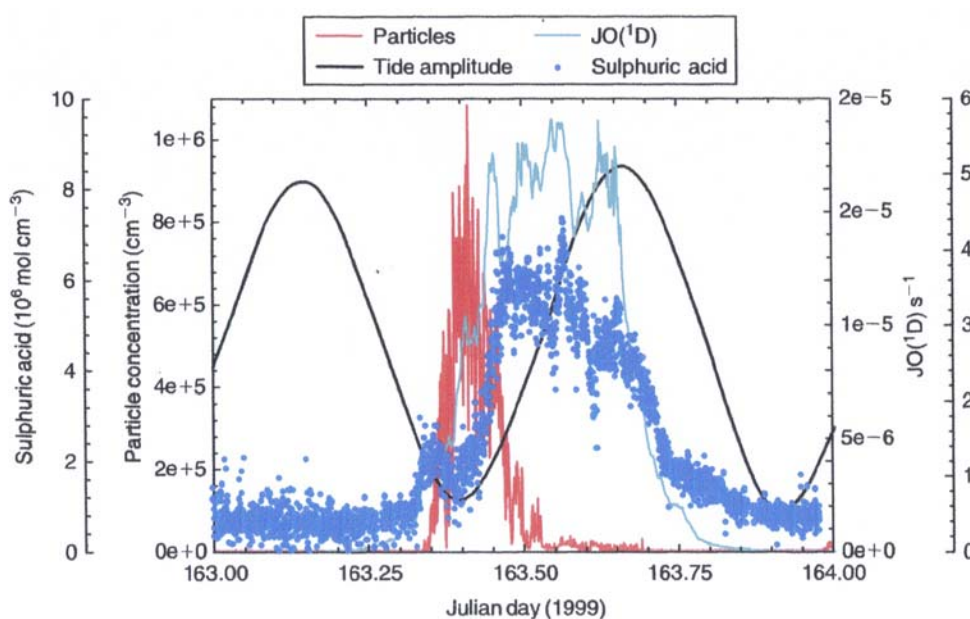
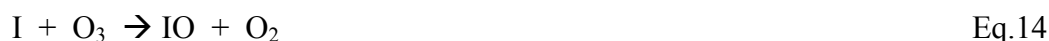


Figure 4: A strong (iodine) nucleation event at Mace Head research station. Notice coincidence with low tide, but slightly before maximum sulfuric acid peak (O’Dowd and Hoffmann, 2005). $JO(^1D)$ is an indicator of radiative intensity.

The nucleation events at Mace Head could not be explained by conventional ternary $\text{NH}_3\text{-SO}_4\text{-H}_2\text{O}$ nucleation physics, which, if it was to be an explanation, required an additional condensing gas to drive $\text{NH}_3\text{-SO}_4$ clusters over the thermodynamic energy barrier to form stable measurable nuclei (Kulmala et al., 2002; O'Dowd and Hoffmann, 2005). The iodine nucleation mechanism originally proposed by Hoffmann et al., (2001) was thus:



As can be seen in Eq.16, I_2O_4 is the basic unit for polymerization of iodine oxides, which can then condense from the gas phase to form nanometer sized aerosols. The basic unit has been of some discussion however, with Saunders and Plane, (2005) suggesting that I_2O_5 may be the basic unit, formed by sequential oxidation of I_2O_2 by O_3 :



This sequence was shown to be thermodynamically favorable, although I_2O_5 is relatively soluble, which does not fit well with the hygroscopic data measured for 8 nm particles at Mace Head by UF-TDMA (Ultrafine Tandem Differential Mobility Analyzer). UF-TDMA data from Mace Head showed that particles formed during nucleation events were quite insoluble, with growth factors at 90 % relative humidity of about 1.1 (Väkevä et al., 2002). This is more inline with I_2O_4 . The basic monomer unit is therefore yet to be fully elucidated.

Once nucleation was found to occur in the laboratory it was then necessary to determine if iodine emissions were large enough in the field to produce the observed nucleation events. It was thought that the large beds of macro algae, such as *Laminaria digitata*, were responsible for the iodine emissions due to their very high iodine concentrations and previous work showed significant fluxes of volatile iodocarbon compounds from the inter tidal region (Carpenter et al., 1999). Incubation studies showed that, indeed, exposure of algae species found around Mace Head to light and ozone could lead to significant particle production (McFiggans et al., 2004; Sellegri et

al., 2005). However, it was also found that I_2 , rather than iodocarbon compounds, was the major source of gas phase iodine species, contributing some orders of magnitude more iodine radicals to the atmosphere than CH_2I_2 ; the compound previously thought responsible for iodine nucleation at Mace Head (McFiggans et al., 2004; McFiggans, 2005). Indeed, around the same time I_2 was identified at the site by LP-DOAS (Saiz-Lopez and Plane, 2004) and has since been backed up by additional studies (Peters et al., 2005 and refs. therein). The laboratory study by McFiggans et al., (2004) also appeared to confirm the nucleation mechanism, with direct identification of IO fragments by AMS, which agreed very well with laboratory produced spectra using synthetic I_2 (Figure 5). While this all appears to agree quite well with the iodine oxide nucleation hypothesis, there have also been some anomalous findings. For example, particles produced by Caine et al., (2007a) also in a chamber containing a macro algae species at Cape Grim Tasmania, Australia, were only stable when collected on plates coated with xylene, suggestive of an aromatic compound. Unfortunately more robust speciation techniques for nucleation size aerosols are hampered by a method that can collect enough mass of nm-sized aerosols for offline analysis. On-line analysis techniques (e.g. AMS) have a lower aerodynamic diameter cutoff of about 30 nm, and therefore also cannot currently be used for iodine speciation in nucleation size aerosols. While iodine nucleation events have been observed at Mace Head, there is very little work in other locations. Moreover, despite rather extensive macro algae beds at Cape Grim, Tasmania, no iodine related nucleation has been observed (Caine et al., 2007b). Nucleation events have been noted in Antarctica, the Great Barrier Reef and a number of other coastal areas, and therefore it is vital to determine if these events are related to iodine chemistry, sulfur chemistry or some other unknown mechanism (Bigg and Turvey, 1978; Broadbent and Jones, 2004; Jones and Trevena, 2005; Yoon et al., 2007).

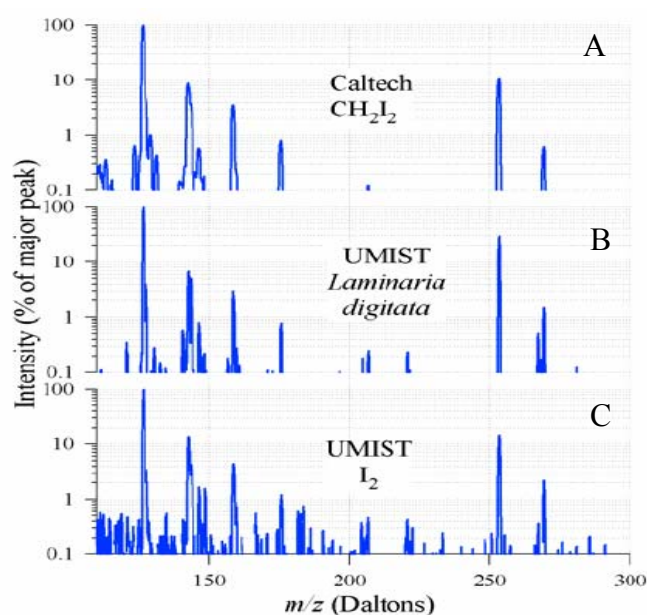


Figure 5: AMS spectra of (A) particles produced by synthetic CH_2I_2 in the Caltech chamber, (B) particles produced from *Laminaria digitata*, (C) particles produced by I_2 (McFiggans et al., 2004).

There is a significant amount of research that has, and continues, to go into elucidating iodine gas phase chemistry and sources. Unfortunately, very little research has been conducted on iodine speciation within aerosols, rain, or snow. Iodine speciation in the atmospheric aqueous phase has large implications for verifying gas phase reactions and assumed reactions that occur within the aerosols as employed in models (McFiggans et al., 2000; Pechtl et al., 2007). Moreover, it has been hypothesized that aerosols may contribute to gas phase iodine chemistry through degassing, for example by Eq.5 and 6 (McFiggans et al., 2000) and therefore knowledge of speciation within aerosols is vital in predicting how important these reactions will be.

As noted above, iodine should theoretically exist in aerosols as iodate, as IO_3^- is believed to be chemically stable in the atmosphere. In most existing models iodate is treated as the iodine sink species and once it is formed it is essentially removed from atmospheric cycles (Vogt et al., 1999; McFiggans et al., 2000; Pechtl et al., 2006). Moreover, iodide should be oxidized at diffusion-controlled rates ($\sim k=5 \times 10^9$) to species such as HOI and XI, and therefore should be well below current detection limits. However, as will be highlighted throughout the atmospheric section of this thesis (e.g. Gilfedder et al., (2007b)), there is very little evidence of iodate dominance in field samples and strong evidence for the presence of iodide. Moreover, it is also likely that non-volatile organic iodine species play a significant role in iodine speciation in the aqueous phase (Baker et al., 2001; Baker, 2005; Gilfedder et al., 2007a,b,c Pechtl et al., 2007). For example, Baker, (2005) found during 2 extensive cruises of the Atlantic ocean (both northern and southern hemispheres) that iodate, iodide and organically bound iodine were present in both fine mode ($< 1 \mu\text{m}$) and coarse mode ($> 1 \mu\text{m}$) aerosols. The organically bound iodine was concentrated in the fine mode, whereas iodate was predominantly in the coarse mode particles. Gilfedder et al., (2007b) also found direct evidence of organic iodine species (although all were unidentified except for iodoacetic acid) in IC-ICP-MS chromatograms, in addition to the calculated organically bound fraction.

1.1.4.3 Precipitation

Precipitation is the only source of fresh water for the terrestrial environment. It also plays vital roles in shaping the earth, via processes such as erosion, and governing spatial distribution of ecological systems. No living animal can live without the input of precipitation, albeit that some organisms have been able to evolve some very nifty characteristics to cope with water scarcity. It is interesting to note then that all water droplets are water vapor condensed on aerosols, and that the properties of the aerosols (e.g. size and chemistry) affect the efficiency of this condensation. This is concisely given by Köhler theory, but a thorough description is out of the scope of this thesis and interested readers are direct to the recent review by McFiggans et al., (2006). It is

sufficient to note that the chemistry of the aerosol will influence the probability of droplet formation. Importantly, iodine in precipitation is most likely transferred directly from the aerosol to the droplet during aerosol activation (Gilfedder et al., 2007b). This represents an important pathway for iodine transfer from the oceans to the continents, where it is a vital nutrient for all mammals (to be discussed later) (Fuge and Johnson, 1986). As such, it is important to know the processes that are occurring within each aerosol and droplet (particularly speciation) as well as the processes that effect the bulk iodine concentration within clouds.

Iodine levels in rain and snow generally range between 0.2-10 $\mu\text{g l}^{-1}$ (1.6-78 nmol l^{-1}), and do not appear to depend strongly on distance from the ocean, but decrease rapidly with increasing elevation (Truesdale and Jones, 1996; Moran et al., 1999; Baker et al., 2001; Gilfedder et al., 2007c). It must be noted however, that so-called total iodine levels given by various authors may be dependent on analytical methods. For example, Campos et al., (1996) assume that the sum of inorganic species (iodide and iodate) is equal to total iodine, and Neal et al., (2007) use a UV-Vis-spectrometric method that integrates inorganic iodine as well as an unknown fraction of organically bound iodine (Wong and Cheng, 1998). There are a growing number of studies that increasingly hint at the importance, or indeed dominance, of organically bound iodine in both marine (Baker et al., 2001; Gilfedder et al., 2007b) and continental (Gilfedder et al., 2007a,b,c) precipitation and thus interpretation of total iodine levels must also consider the analytical method employed for quantification. The most reliable method for total iodine analysis is currently inductively coupled plasma mass spectrometry (ICP-MS), which decomposes all iodine species to I^+ (plasma temperatures ca. 6000K) before quantification with the mass spectrometer.

The discussion above also highlights that accurate speciation of iodine is necessary when attempting to reconstruct iodine cycling in the atmospheric aqueous phase. Due to the low concentrations of individual iodine species typically found in precipitation (less than 1 $\mu\text{g l}^{-1}$; 7.9 nmol l^{-1}), it is often difficult to achieve satisfactory accuracy and precision with the few methods that do exist. Current techniques include square wave voltammetry, differential pulse polarography, UV-Vis spectroscopy, and ion chromatography-ICP-MS with differing sensitivities and difficulties (Truesdale and Spencer, 1974; Luther and Cole, 1988; Campos et al., 1996; Biester et al., 2004; Gilfedder et al., 2007c). Undoubtedly, whichever method is applied it must at least be able to measure iodide, iodate and total iodine. Currently all measurements of iodine speciation in precipitation have been made at coastal locations, and especially in Britain (Truesdale and Jones, 1996; Campos, 1997; Baker et al., 2001). These studies found that about half of inorganic iodine was iodate and half was iodide. However, Baker et al., (2001) showed that organic iodine may compose a significant fraction of the total iodine, and that speciation depended on air mass origin.

The presence of iodide in precipitation (as mentioned above for aerosols) is currently an anomaly that cannot be reproduced by models due to iodide's theoretical very rapid oxidation kinetics. When this is combined with the observation of organic iodine and lack of iodate it points to a large gap in the current knowledge of aqueous phase iodine speciation in the atmosphere.

1.1.5 Terrestrial environment

Iodine enters the terrestrial environment via precipitation. It was historical thought that once in terrestrial systems the halogens (F, Cl, Br and I) behave conservatively, meaning they reacted only very sparingly with their surroundings. Indeed, the parameter 'adsorbable organic halogens (AOX)' was, and in some cases still is, used to quantify organic halogen compounds thought to be purely from anthropogenic sources (Müller, 2003). However, in the last 15-20 years or so, it has become increasingly apparent that the halogens do not behave conservatively, and that organic halogen compounds form by natural (not related anthropogenic pollution) means (Asplund and Grimvall, 1991; Müller et al., 1996; Müller, 2003; Schöler et al., 2003). Natural formation of organohalogens can occur biologically by haloperoxidase and other similar enzymatic reactions (e.g. Gribble, 2003), or, as shown by Schöler and Keppler (2003), through abiological mechanisms involving Fe. In this abiotic catalytic system Fe^{3+} is reduced by organic matter, Fe^{2+} can then oxidize iodide to I_2 , which will then react with the abundant organic matter in the soil to form organoiodine compounds such as Me-I. The Fe^{2+} is reoxidised to Fe^{3+} and the cycle may then start again. Natural abiotic formation of organohalogens has even been shown to have occurred in the primordial solar system, with identification of organochlorines in carbonaceous chondrites (Schöler et al., 2005).

Iodine is of vital importance for ecological systems on the continents, as all mammals (including humans) require a dietary iodine intake for correct function of the thyroid gland. Insufficient iodine may lead to some severe and debilitating diseases and syndromes, such as goiter and most devastatingly, cretinism. As summarized by Slavin, (2005), cretinism is a lifelong mental and physical retardation, acquired while in the womb, by insufficient iodine intake by the mother. Health issues derived from lack of iodine are related to the production of two hormones, thyroxine and triiodothyronine, that are responsible for maintaining the metabolism at a basal rate and building nerve cells in the brain. While goiters (enlarged thyroid) are often an outward sign of iodine deficiency, the goiter itself is not of large health concern. Rather, it is the other syndromes caused by iodine deficiency, which the goiter signifies, that has led to the World Health Organization listing iodine deficiency disorders (IDDs) "as the world's most prevalent, yet easily preventable, causes of brain damage" (<http://www.who.int/nutrition/topics/idd/en/>). Iodine deficiencies do not only affect less developed countries (Figure 6). More developed countries, such

as France and Ireland (despite the iodine emissions mentioned above!) are currently listed as iodine deficient (Andersson et al., 2007). Indeed insufficient iodine intake by school children between 6-12 years is currently at 22.2 million pupils (42 % of school children) in Europe alone (Figures 7) (Andersson et al., 2007).

The distribution of iodine deficiency has been associated with many causes since it was first noted by the Romans in populations of the European Alps (Slavin, 2005). There was even a time where a goiter was seen as common place in Europe, and even attractive when only slightly enlarged (Andersson et al., 2007). It has been commonly associated with drinking water from mountainous regions and limestone bedrock, although to date there is very little scientific evidence for a direct relationship between these factors and goiter (Fuge and Johnson, 1986; Slavin, 2005). To date IDD's appear to be multifaceted, with contributions from genetics (inbreeding particularly enhances the prevalence of IDD, as observed in Derbyshire England (Slavin, 2005)), lack of selenium and compounds known as goiterogens that inhibit the uptake of iodine. Currently the major source of iodine for more industrialized nations and some of the less industrialized countries is iodine supplements added to salt.

Natural sources of iodine are particularly important in areas that do not currently have access to iodine supplements, or rich iodine sources such as fish, seaweed, and milk. The iodine in milk may not only originate from grass, which generally has low iodine levels, but also from direct ingestion of soil by bovine. Therefore it is also important from a health prospective to understand the natural iodine cycle and the major reservoirs of iodine in the terrestrial environment. It is particularly important to understand iodine speciation in this regard, as some iodine compounds are beneficial to health (such as the inorganic species), while others are detrimental (such as the carcinogenic iodoacetic acid (Plewa et al., 2004)). It seems that the health benefits of iodine bound to dissolved humic material is currently unknown. Therefore it is vital not just from a geochemical perspective, but also from a health perspective to understand how these substances cycle through the environment, and in particular the processes effecting their concentrations. Indeed, as shown by Gilfedder et al., (2007d), humic bound iodine is the dominant species in fresh lake waters from the Black Forest, and so organic iodine species will need to be further investigated by public health departments if a better understanding of the causes of iodine deficiencies are to be understood.

**Degree of Public Health Significance of Iodine Nutrition
Based on Median Urinary Iodine**

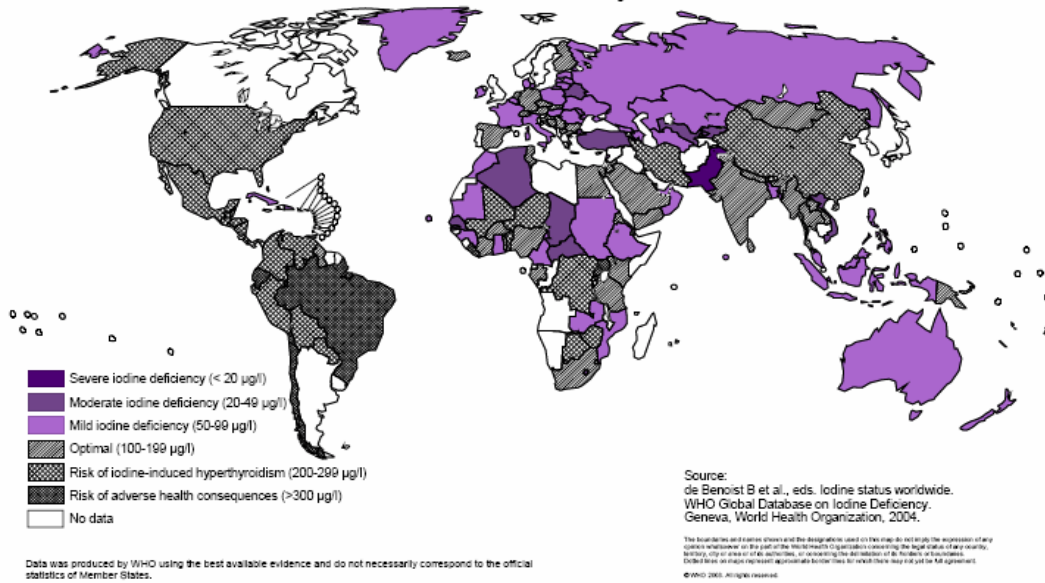


Figure 6: Global iodine intake status (de Benoist et al., 2004).

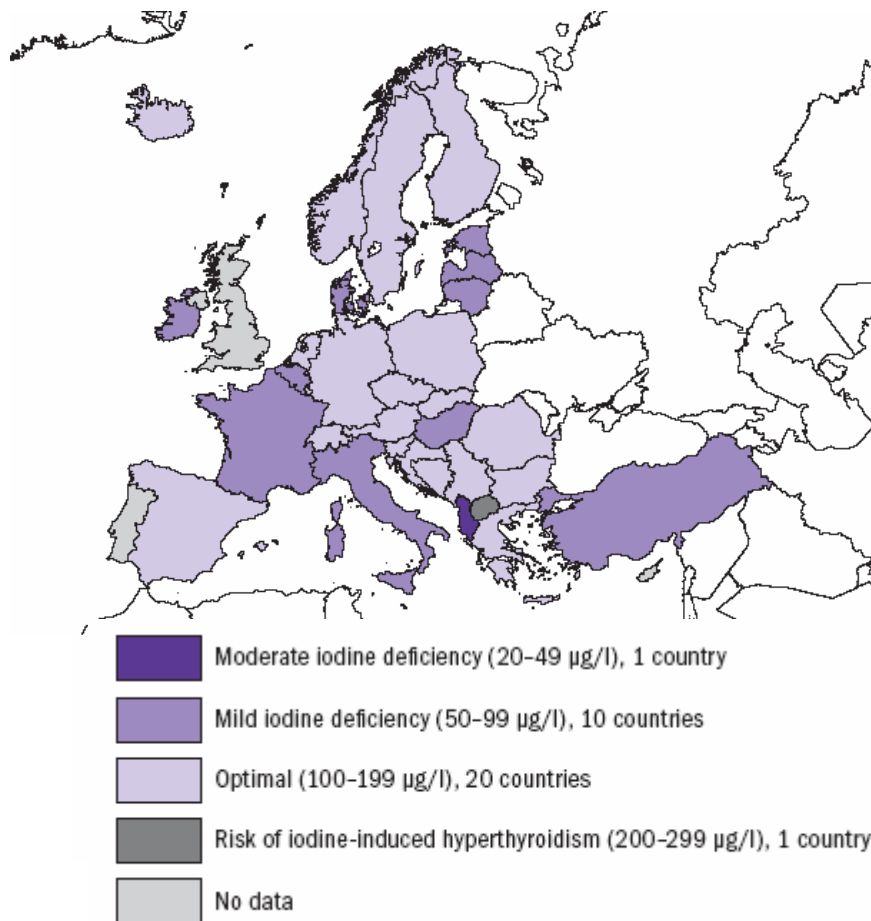


Figure 7: Iodine deficiency status in Europe (Andersson et al., 2007).

A second important initiative to research iodine cycling in the terrestrial environment has only arisen since the nuclear age. During nuclear fission a series of radioactive iodine isotopes are

produced (approximately 20) by the decay of ^{238}U . The two most important radioactive isotopes of iodine are ^{129}I (half life ~ 15 Ma) and ^{131}I (half life 8 days). Iodine-129 is only a low energy beta and gamma emitter, and therefore is currently of little health threat. However, because of its high mobility and volatility it is becoming a widespread anthropogenic radionuclide (Moran et al., 1999; Raisback and Yiuo, 1999; Oktay et al., 2001; Michel et al., 2002; Moran et al., 2002a; Reithmeier et al., 2006). For example, Snyder and Fehn, (2004) have observed ^{129}I transport from the nuclear reprocessing facilities at La Hague (France) and Sellafield (England) from the North to the South Pole. Interestingly, because of its near-zero natural abundance, it has also become a useful tracer for natural processes, such as ocean currents (Santschi and Schwehr, 2004). In contrast to ^{129}I , ^{131}I is a high-energy nuclide, and therefore presents a significant health risk following release of radioactive material into the environment, such as occurred during the Chernobyl accident. One of the primary concerns with ^{131}I is that it accumulates in the thyroid gland due to iodine's status as a nutrient. It then poses a significant threat of thyroid cancer. A thorough review of the radiological and geochemical properties of iodine isotopes is outside the scope of this thesis and the interested reader is direct to texts such as Szidat et al., (2000), Snyder and Fehn, (2004), Moran et al., (2002a) and refs. therein.

Given the above importance of iodine in the terrestrial environment, it is unfortunate that scientific observations have generally been much less systematic than in the atmosphere, with few long-term or collaborative wide-ranging studies. The iodine cycle in the terrestrial environment must, of course, start with rocks and soils. Iodine concentration in rocks is usually very low, less than a few mg kg^{-1} and generally less than 1 mg kg^{-1} , unless there is a significant amount of organic matter present. The highest concentrations are associated with hydrocarbon deposits due to the elevated concentration of organics in these strata. One of the primary factors effecting iodine's distribution in minerals is its large ionic radii and as such iodine does not easily substitute into the crystal lattices of most minerals. It is currently thought that the small iodine concentrations present in rocks is as a heteroatom, in essence 'floating' within and between crystal structures or sorbed on crystal edges and defects. Iodine concentrations in most common rock types is listed by Fuge and Johnson, (1986) in the order: recent sediments > carbonates and shales > sandstones > igneous rocks. More recent work by Muramatsu and Wedepohl, (1998) have shown this to be approximately true, but also show that metamorphic rocks are higher in iodine than igneous but lower than sedimentary rocks. They suggest that iodine is degassed from the sedimentary rocks during subduction, and particularly during high temperature melting associated with igneous rock formations. This appears to be consistent with very high concentrations of iodine and bromine measured in volcanic plumes (von Glasow and Crutzen, 2007). It has been suggested on numerous occasions that the high iodine content in sedimentary rocks is a result of their biogenic origin, a

fact highlighted by iodine's association with organic rich deposits (such as oil and coal). A summary of the iodine content in rocks and their relative contribution to the total crustal iodine inventory is shown in Table 1.

Table 1: Iodine inventory for the earth's crust (redrawn from Muramatsu and Wedepohl, 1998).

Bulk continental crust (2.13×10^{19} t)	Thickness	Crustal units	Subunits	Average concentrations (ppb I)		Average concentrations (ppm Cl)		Cl/I Ratio x1000
	2.9 km =7.3 %	Sedimentary rocks	56 % Shales 26 % Sandstones 18 % Limestones	1800 136 2500	1490	1100 1340 720	2850 ⁺	1.9
10.4 km =26 %	Felsic intrusive magmatic rocks	50 % Granites 50 % Granodiorites and Tonalites	4 7.2	6	280 280		46.7	
1.3 km =3.3 %	Mafic intrusive magmatic rocks			9		190	21.1	
6.3 km =	Metamorphic rocks of the upper crust	64 % Gneisses 15 % Mica schists 18 % Amphibolites 3 % Marbles	24 25 23 31	24	320 320 300 300	316	13.1	
15.8 %								
11.9 km=29.8%	Felsic granulites of lower crust			12		330	27.5	
7.2 km=18 %	Mafic granulite of lower crust			9		70	7.8	
40 km	Bulk continental crust			119		448	3.8	

+ Including 2.8×10^{15} t Cl in evaporates.

It has long been established that rock weathering has only a minor effect on iodine concentrations in soils, the dominant source being atmospheric input (Fuge and Johnson, 1986). As observed in rocks, iodine concentrations in soils also vary widely, and depend on many chemical and physical factors such as pH, Eh, drainage, climate, clay content, and most importantly organic matter content. The combined effects of these factors has been shown in the long term study (25 years) by Neal et al., (2007). An increase in stream water iodine levels over the last two decades was a result of 'wetting-up' of the soil and subsequent decrease in Eh and increase in DOC release. The role of organic matter in binding iodine can best be seen by iodine concentrations in peatlands, where concentrations can be 10's of mg kg^{-1} (Biester et al., 2004), porewater levels in excess of $20 \mu\text{g l}^{-1}$ (Biester et al., 2006) and retention of input in approximately of 50 % (Keppler et al., 2004). However, the sorption capacity of most soils (excluding peat) is also strongly dependent on iodine speciation, with very little sorption of iodide by clays and iron (oxy)hydroxides, but significant sorption of iodate (Neal and Truesdale, 1976; Ullman and Aller, 1980). Unfortunately, the sorption properties of organically bound iodine are hindered by the unknown organo-I species in soils and soil solutions and as such are currently unknown. Iodine may also be lost from the soil as volatile species such as methyl iodide and other polyhalomethanes formed during biotic or abiotic degradation of natural organic matter (Keppler et al., 2000; Schöler and Thiemann, 2005). This represents a feedback cycle to the atmosphere that has largely been overlooked and must be further elucidated in the future.

Iodine levels in streams are usually less than $10 \mu\text{g l}^{-1}$, although some higher levels have been noted in arid and semi-arid environments or groundwater draining organic rich (e.g. coal) deposits (Neal et al., 1990; Andersen et al., 2002; Moran et al., 2002b; Laurberg et al., 2003; Snyder and Fehn, 2004; Atarashi-Andoh et al., 2007; Neal et al., 2007). While the number of studies quantifying total iodine is relatively numerous, iodine speciation and cycling are infrequent, particular over longer time scales. The work of the Heumann group from Mainz, Germany, is an exception, as they have developed numerous hyphenated ICP-MS methods for iodine speciation (see review paper by Heumann et al., 1998). Method development is vital; however without sustained (temporal) use there is no way to gain an understanding of iodine's behavior in the environment. Rather, it gives a 'snap shot', that may just be a transitory state. Work by the Haumann group has, however, shown using IC-ICP-IDMS, HPLC-ICP-IDMS and SEC-ICP-IDMS that iodine in terrestrial aqueous systems is mostly bound to organic matter, and that microbiological transformations may be important (Reifenhäuser and Heumann, 1990; Rädlinger and Heumann, 1997; Heumann et al., 1998; Rädlinger and Heumann, 2000). Iodine was also found to be bound covalently to humic organic matter by electrospray-mass spectrometry and synchrotron techniques in groundwater samples (Moulin et al., 2001; Reiller et al., 2006; Schlegel et al., 2006). So far there is little consensus on the exact organo-iodine species, with most authors being content with an organo-I fraction. Some evidence exists for an aromatic iodine species (Moulin et al., 2001; Schlegel et al., 2006), although iodophenols cannot be responsible for the bulk of organo-I (Wuilloud et al., 2003).

The only long-term study on iodine speciation and cycling in the terrestrial aqueous environment is from Jones and Truesdale, (1984). These authors essentially monitored inorganic iodine speciation and cycling in two British lakes over a 14-month period. They found that iodide increased in the hypolimnion during anoxia, but could not derive whether it was from the sediments or lake water column. They also noted that in the epilimnion of both lakes IO_3^-/I^- ratios were significantly out of equilibrium, as noted for the marine environment. It was suggested that the disequilibrium was related to biological reduction of iodate. Jones and Truesdale, (1984) also suggested that iodine behaved as a micronutrient, conforming to Redfield-like ratio with an I/C mass ratio of about 1×10^{-4} . Similar values were found in sediment trap samples from the lakes district, UK, supporting iodine's possible role as a micronutrient (Pennington, 1974).

1.2 Aims of this work

The aim of this project was essentially to gain a more holistic understanding of the aqueous iodine cycle in the atmosphere (i.e. rain, snow, and aerosols) and terrestrial hydrosphere (lakes and streams). In particular, direct observation of iodine speciation (including inorganic and organic

iodine species) and temporal changes in speciation were seen as vital in gaining a more thorough understanding of iodine systematics. This was in part due to the observation that despite the fact that iodine oxides are theoretically the only sink specie in the atmosphere, very little field observations currently exist to confirm model predictions. The temporal component in iodine cycling in lakes was also especially interesting, as no long-term study in freshwaters has been undertaken since Jones and Truesdale, (1984). Moreover, the behavior and cycling of organically bound iodine in lake is currently unknown, despite iodine's vital importance as a micronutrient and previous work showing that the proportion of organically bound iodine is significant. Indeed, this is also important from a health perspective, as uptake efficacy studies have mostly focused on the inorganic species and there is little knowledge of organic iodine species ability to relieve IDD. It also must be noted that the work evolved significantly during the three years of study; most importantly the cooperation with Senchao Lai and Professor Thorsten Hoffmann from the University of Mainz in the second and third years allowed a much deeper understanding of atmospheric processes in terms of iodine speciation in aerosols and precipitation.

A second aim was to develop a cheap, sensitive, and rapid method for iodine quantification in sediments and soils which could even be applied in the basic laboratories often found in less developed areas where IDD is most prevalent. This arose during the doctoral work, as, unfortunately, the most common technique for total iodine quantification in solid samples is neutron activation analysis, which requires access to a nuclear reactor and is expensive to commission.

The thesis is broken into 2 primary chapters and 2-3 sub-chapters. Each of the sub-chapters are manuscripts that have either been published (3) or submitted (2) to internationally recognized journals:

- **Chapter 1 - Atmosphere**
 - 2.1 Iodine speciation in rain and snow: Implications for the atmospheric iodine sink (Published in *Journal of Geophysical Research: Atmospheres*)
 - 2.2 Iodine and Bromine speciation in snow and the effect of orographically induced precipitation (Published in *Atmospheric Chemistry and Physics*)
 - 2.3 Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to droplet phases (Submitted to *Atmospheric Chemistry and Physics* 2008)

- **Chapter 2 - Terrestrial**

- 3.1 A thermo extraction–UV/Vis spectrophotometric method for total iodine quantification in soils and sediments (Published in *Analytical and Bioanalytical Chemistry*)
-
- 3.2 Iodine speciation and cycling in limnic systems: observations from a humic headwater lake (Mummelsee) (Published on-line in the discussions forum of *Biogeosciences*)

1.2.1 Methods

The largest difficulties in determining iodine speciation in aqueous samples are firstly the very low levels of individual iodine species and, secondly, being able to unequivocally quantify total iodine. Previous methods, such as square wave voltammetry are sufficient for oceanic samples, but are not sensitive enough for terrestrial freshwater iodine levels (Cook et al., 2000). Spectrometric methods can presumably (effects induced by addition of chemicals on organo-I are unknown) quantify iodate, but not iodide. As pointed out recently, quantification of total iodine in aqueous samples is also not such an easy procedure due to the complex and refractory nature of natural dissolved humic material (Schwehr and Santschi, 2003). They propose a complex and time consuming procedure to completely destroy carbon-iodine bonds, however such procedures are circumvented by the use of ICP-MS. ICP-MS can unequivocally determine total iodine due to plasma temperatures higher than 6000 K, and quantification by mass spectrometry. The major benefit of ICP-MS is the very low detection levels, and its element selective technique. Also, this technique has become a routine procedure in many laboratories, and as such most interferences and complications are known and can be accounted for (for example, mass interferences). For aqueous speciation we have employed normal mode ICP-MS for total iodine quantification, and coupled an ion chromatograph (IC) to the ICP-MS for iodine speciation. An example of an ion chromatograph of rain and aerosols from Mace Head Ireland using an anion exchange resin is shown in Figure 8. Organically bound iodine is calculated as total iodine minus the inorganic species, iodide and iodate. IC-ICP-MS has been used by various workers (e.g. see Heumann et al., (1998)), however the combination used here is significantly more sensitive due to the introduction of a Meinhard nebulizer and cyclone spray chamber as well as a column that produces very good peak shapes (Dionex AS16 column with an AG16 guard column). The column is particularly important in gaining precise results at low detection limits. An estimated detection limit of 30 ng l⁻¹ was obtained for inorganic iodine species using this combination. Accuracy was checked by running standard reference material BCR-611, which is a groundwater sample with iodine levels of about 9.4 µg l⁻¹.

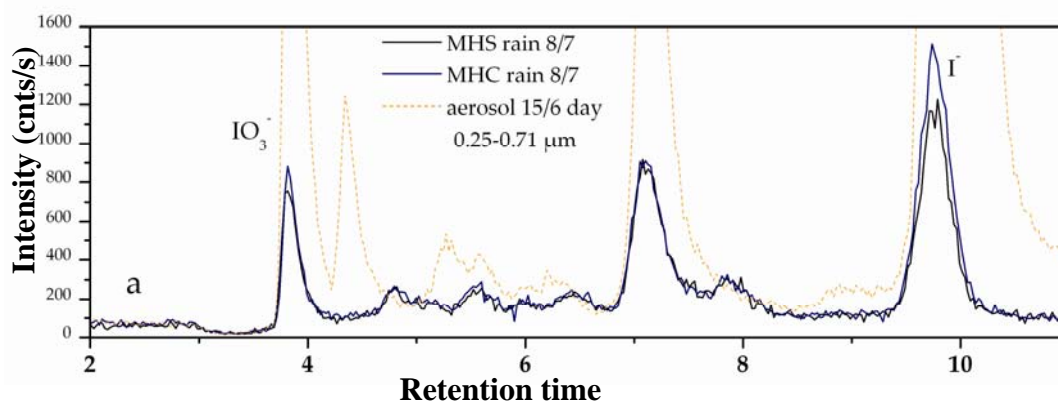


Figure 8: Typical anion chromatograph of rain samples from Mace Head (MHC and MHS) and aerosols also sampled from Mace Head using a Birner cascade impactor. The iodate peak in the rain samples contains approximately 1.8 nmol l^{-1} . The peak in the middle is an unidentified, presumably organic, iodine species.

The second major aim of this work was to develop a method for total iodine analysis in soils that is cheap, but also accurate and precise with low detection limits. Iodine was thermally extracted in an AOX machine at $1000 \text{ }^{\circ}\text{C}$ and the released gases were trapped in Milli-Q water and analysed by UV-Vis spectrometry. Weighed soil or sediment samples (8-300 mg) were placed into the automated injection system of the AOX machine and injected at a rate of 2 mm s^{-1} , dried at the edge of the furnace and then moved into the primary combustion section. The released gases were carried by O_2 (which also assisted with combustion of organic matter) into the trapping apparatus (previously the sulfuric acid bubbler of the AOX). The iodine, trapped in Milli-Q water, was decanted into a Falcon tube and filled to the nearest marker, generally about 12 ml. This was then analysed by a kinetic photolytic method, whereby iodine quantitatively catalyses the reduction of orange coloured Ce^{4+} and oxidation of As^{3+} . The rate of this reaction is determined as absorbance at $\lambda = 432 \text{ nm}$ at a pre-selected reaction time. Generally 10 or 15 minutes were sufficient for iodine concentrations in solution between $10\text{-}150 \text{ } \mu\text{g l}^{-1}$. The spectrometric method was calibrated with iodide standards and the entire method was checked by burning two soil standard reference materials and one stream sediment material. After optimization the method was found to be accurate and very precise with relative standard deviations of less than 5 % for samples and standard reference materials.

One of the complicating factors in determining the detection limit in this method, as pointed out by Michel and Villemant, (2003), is that by increasing the mass of sample burnt in the furnace increasingly lower detection limits can be obtained. We overcame this problem by adapting a statistical approach, whereby a selection of masses of reference material NCS DC 73312 were burnt in the furnace and the absolute iodine levels were plotted verses \ln transformed absorbance. By fitting confidence limits to this graph we were able to calculate the minimum absolute detection limit rather than on a per-mass basis. The statistical procedure is described in Clayton et

al., (1987) and DIN 32645, (1994). The major benefit is that the detection limit is calculated with a known statistical certainty; we opted for 95 % confidences, instead of the more common ‘3 times the standard deviation of the baseline’ as this only has a confidence of 50 %. The calculated detection limit was then 49 ng iodine, which is sufficient for iodine quantification in most geological materials.

1.3 Summery of Findings

1.3.1 Iodine speciation in rain and snow: Implications for the atmospheric iodine sink

This first paper describes 11 months of precipitation (rain and snow) measurements from Lake Constance (Überlingen), and more transitory measurements from the Black Forest (snow and rain), the Alps (rain and a glacier ice core) and Patagonia (rain from Biester et al., (2004)). It also outlines the IC-ICP-MS method used for iodine speciation. As noted in the literature section, iodine oxides are predicted as the only stable sink species for iodine in aerosols and precipitation, with other species being only short-lived transitory oxidation states. It was found that total iodine levels in rain were considerably higher than in previous studies that had only quantified inorganic iodine species and assumed that this was total iodine (e.g. Truesdale and Jones, 1996). The discrepancy was due to the presence, and indeed dominance, of organically bound iodine, which at Lake Constance made up on average 54 % of the total iodine, followed by iodide (27 %) and finally iodate (~10 %). Moreover, organically bound iodine was also found to be the most abundant iodine fraction at all of the sample locations. One of the implications of this was that significant correlations were found between total iodine, Na and Br whereas previous studies had found no relationship between these elements (e.g. Campos et al., 1996). Significantly, organically bound iodine is currently not parameterized in any atmospheric iodine models (Vogt et al., 1999; McFiggans et al., 2000), with only the study by Pechtl et al., (2007) including any iodine-organic reactions. These authors found that reduction of iodine species such as HOI could aid in maintaining iodide levels, which are currently an anomaly due to theoretically very fast oxidation kinetic (diffusion controlled).

In addition to the organically bound fraction described above, up to 5 unidentified peaks were found in IC-ICP-MS chromatograms from all sampling locations (Figure 9). These species must be organic due to the short lifetime of all other inorganic iodine species and anionic due to the consistent separation by the anion exchange column.

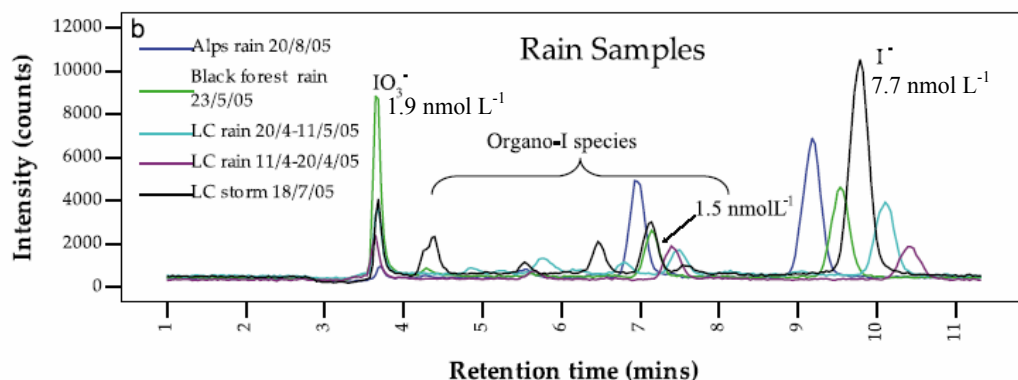


Figure 9: Typical IC-ICP-MS chromatograms in rain from various locations.

As found by previous studies, iodine in precipitation was strongly enriched in rain and snow relative to ocean water (based on I/Na ratios) by 280-2100 times (Winchester and Duce, 1967; Woodcock et al., 1971; Moyers and Duce, 1972; Baker et al., 2001). This highlights that, in contrast to the other halogens, aerosols and precipitation act as a net sink for iodine rather than a source. This extra iodine undoubtedly stems from oceanic biogenic iodine emissions, with perhaps minor sources from the terrestrial environment. It is concluded that iodine organic matter interactions must be included in models, and that such reactions could have significant implications for atmospheric chemistry such as ozone depletion.

1.3.2 Iodine and Bromine speciation in snow and the effect of orographically induced precipitation

The effect of distance from the ocean is one of the controversies that currently obscure a better understanding of processes relating to iodine levels in precipitation. There have been some authors that favor a strong iodine gradient from the ocean inland (Fuge, 2005), while other workers have found little or no effect of distance from the ocean (Krupp and Aumann, 1999; Moran et al., 1999). The aims of this paper were to assess the effect of orographically induced precipitation on iodine levels in snow from the Black Forest and quantify the dominant iodine species in snow from this region. The study site in the northern Black Forest was chosen explicitly to extenuate orographic effects while minimizing horizontal distances. A transect was chosen between Ottenhöfen (326 masl) and Hornisgrinde, the highest mountain in the northern Black Forest (1164 masl). Samples were taken at different heights between these two endpoints and analysed for total iodine and iodine speciation. Prior to sampling the air mass had advected from the west over the mountains.

It was found that orographically induced precipitation had a large and significant effect on iodine levels in snow; with total iodine levels more than halving over the 840 height meter transect (38 to 13 nmol/l). Iodine levels decreased expediently for all species over the transect, with regression coefficients higher than 0.77 and all were statistically significant ($p < 0.001$). As such it was

suggested that orographically induced precipitation has a significant influence on iodine levels and iodine transport inland. Moreover, the conflicting reports by other workers may be due to orographic effects at the different sampling sites rather than to horizontal distance from the ocean.

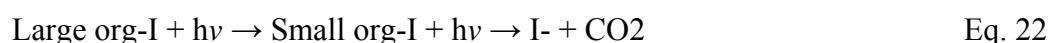
As found in the first paper organically bound iodine was the dominant species in all snow samples, making up 61-75 % of the total iodine levels. Iodide was the next most abundant species, while iodate was below detection limits in nearly all samples. It is thought that the majority of the organic iodine is of high molecular weight, which is not eluted from the column or contributes to the baseline. Two of the unidentified anionic species observed in IC-ICP-MS chromatograms described in the first paper were also found in all snow samples in the Black Forest, and also decreased in concentration with increasing altitude. As observed in other studies iodine was highly enriched relative to the ocean ($EF > 130$), increasing linearly until 796 masl, after this point the pattern was not so clear. Significant correlations were noted between iodine and other elements such as Br, Li, V, Mn, Co, Pb, Ba, Sb, and U ($r > 0.82$, $p < 0.001$), suggesting that iodine was internally mixed within the snow crystals and that the orographic effect is a general process affecting all elements.

1.3.3 Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to droplet phases

All precipitation originates from condensation of water vapor on aerosol particles (CCN), and grows both by coalescence and vapor deposition until it gains enough mass to fall against the updraft. As such, we thought it would be interesting to sample aerosols and precipitation in unison and try to trace iodine species from the aerosol phase into the droplet phase. A second aim was to elucidate if the unidentified species observed in rainfall were more widely distributed globally and also if they existed in the aerosol phase. Finally, aerosols were sampled diurnally to try to elucidate day-night differences in iodine speciation. Precipitation samples were collected from Australia, New Zealand, Mace Head, Ireland, Germany, Switzerland, and Greenland. Some of the data from the previous papers (e.g. Patagonia, the Black Forest, and Lake Constance) were also included for comparison between sampling locations. Aerosol samples were taken from Mace Head research station between the 15th June-6 July with a 5 stage Birner cascade impactor and PM 2.5 impactor. One day of PM 2.5 day-night aerosol samples was also obtained from a ship cruise of the Atlantic aboard the *Celtic Explorer*. The aerosol size ranges for the cascade impactor were between 0.085 μm and 10 μm . The filters were extracted with Milli-Q water with ultra-sonification. As in the other papers iodine was analysed by ICP-MS and IC-ICP-MS. Back trajectories for aerosol samples were modeled with the NOAA-HYSPLIT model.

In contrast to current theory, organically bound iodine was by far the dominant iodine species in the aerosol samples from Mace Head, accounting for a median of 91 % during the day and 94 % during the night of total iodine. The dominance of organic iodine was consistent between both impactors and was also observed in the offshore samples. Iodide was the next most abundant species, with iodate levels the lowest of all species in the aerosols.

In terms of day night systematics, we could not observe any significant ($p > 0.05$) day night differences for total iodine, organo-I, or iodate. However, it was found that there was significantly more observations of iodide enrichment during the day compared to the night ($p < 0.05$), and was particularly noticeable in the $< 2 \mu\text{m}$ samples. This could also be seen when each impactor sage was averaged over the sampling period. It was suggested that the organo-I is photolytically degraded to yield iodide, a process support by observations from the marine environment (Wong and Cheng, 1998).



Despite no significant observations of decreased organo-I levels during day, which are implied by Eq. 22, this does not make the suggestion of photolytic disintegration invalid. There are two extra points to consider here, (1) that we have only sampled the water soluble iodine, whereas the majority of organic matter in aerosols at Mace Head is insoluble (O'Dowd et al., 2004), and (2), the major aim at the outset of the study was to trace iodine from the aerosol phase into rain and as such selected sampling days did not have high solar radiation, making it difficult to test Eq.22.

Interestingly, the unknown species previously described in precipitation samples were also observed in high concentrations in aerosols from Mace Head. Indeed, up to 5 unknown peaks were observed in IC-ICP-MS chromatograms. Rain samples taken at the same time as the aerosols also displayed at least the largest of these peaks, indicating that whatever this species is, it is transferred from aerosols into rainfall during aerosol activation. These species were also observed in precipitation from the other sampling locations in both southern and northern hemispheres, suggesting they are globally ubiquitous and are derived from marine aerosols (Figure 10).

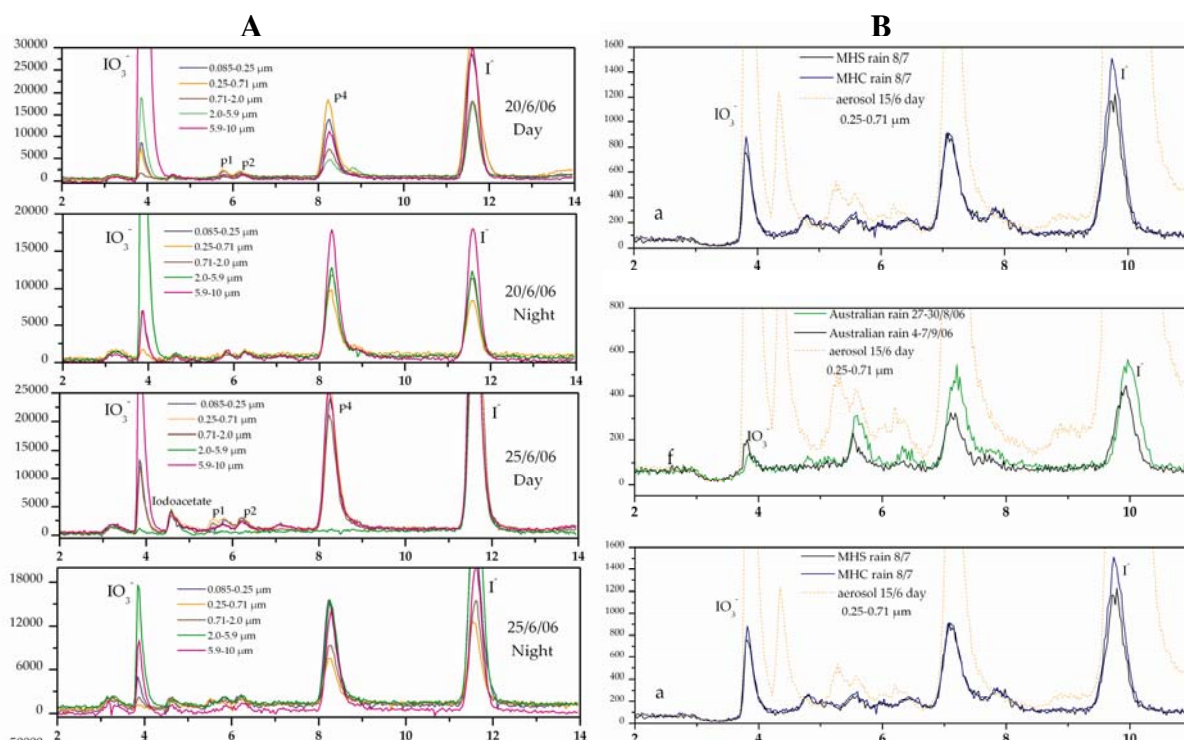


Figure 10: (A) Typical IC-ICP-MS chromatograms of aerosol samples. (B) Typical chromatogram of rain samples from Mace Head Ireland and Australia

As suggested above in Eq.22 it is thought that these species form during the break down of large iodo-organics. This is suggested, but not proved, by significant correlations between iodide and the unknown species.

It is currently thought that the large organic iodine molecules form by reactions between transitory iodine species such as HOI and organic matter derived from the ocean surface microlayer. Typical organic compounds could be proteinaceous microcolloids, which also decay photolytically or by acidification (Chin et al., 1998; Leck and Bigg, 2005; Bigg, 2007; Leck and Bigg, 2007). One area that has not been investigated in detail and warrants further work is interactions between reactive iodine species in the gas phase and organics in the gas phase such as terpenes. Some early work suggested that such reactions may be significant for ice nuclei, decreasing freezing temperatures (Rosinski and Parungo, 1966), but little has been done since this time. It is suggested that dedicated chamber studies are needed to prove or disprove this possibility.

1.3.4 A thermo extraction–UV/Vis spectrophotometric method for total iodine quantification in soils and sediments

This paper is fully discussed in the methods section 1.2.1.

1.3.5 Iodine speciation and cycling in limnic systems: observations from a humic headwater lake (Mummelsee)

Moving from the atmosphere into the terrestrial aqueous iodine cycle, this paper describes one year of iodine cycling and speciation in the Mummelsee. The Mummelsee is a humic rich, Headwater Lake in the northern Black Forest, located at an altitude of 1036 masl, just below the peak of Hornisgrinde. As noted in section 1.6, there are very few studies concerned with temporal changes in iodine speciation (particularly organic iodine) in freshwater limnic systems, and therefore the aim of this study was to identify the most important species and their cycling behaviour under changing redox conditions. Depth profiles were collected from the deepest part of the lake each month (including when the lake was frozen) in 1 m depth intervals, filtered in the field, and transported back to the cool room at the Institute for Environmental Geochemistry, Heidelberg. As above, samples were analysed by ICP-MS and IC-ICP-MS for total iodine and iodine speciation, respectively. In addition, selected redox sensitive metals (e.g. Fe and Mn) were also measured by ICP-OES on acidified filtered and unfiltered samples collected in conjunction with the iodine samples.

Iodine levels in the Mummelsee averaged $1.93 \mu\text{g l}^{-1}$ (15 nmol l^{-1}), which is on the low end of the scale for fresh waters and nearly identical to precipitation at this location (Snyder and Fehn, 2004; Gilfedder et al., 2007c). The majority of iodine in the lake was bound to organics with, on average, $85 \pm 5 \%$ of the total iodine as organo-I. Seasonal changes in organo-I were not pronounced, with a slight increase in the epilimnion during summer and decrease in the hypolimnion during September and October and a total loss of organo-I in the bottom 2 m during May 2006. There also appeared to be a net formation of organo-I during turnover events, when oxygen was mixed into the anoxic hypolimnion.

In contrast to the organically bound iodine, the inorganic species showed pronounced seasonal variation. Iodide was depleted to below detection limits in the epilimnion during the summer and autumn, whereas iodate concentrations continuously increased during the year. This trend was reversed in the hypolimnion during low dissolved oxygen conditions, with strong release of iodide from the sediments into the overlying water column and reduction of iodate. It was suggested that the loss of iodide in the epilimnion was associated with biological uptake and precipitation of detritus to the sediments. This was supported by a sediment core, which displayed high iodine ($11.7 \pm 1.7 \text{ mg kg}^{-1}$) and organic carbon ($>20 \%$) levels and significant correlations between organic carbon and total iodine ($p < 0.001$). Indeed, enrichment factors of sedimentary iodine over water column levels indicate that iodine is enriched by ~ 6600 times, and that the sediments are a net sink for iodine in this lake. The increase in iodate is more perplexing, as most studies are focused on iodate reduction due to the disequilibrium between I^-/IO_3^- discussed above. Oxidation of iodide and other transitory species, while thermodynamically favorable, are not kinetically

plausible (Luther et al., 1995). Indeed, even in ocean surface waters with very high Eh, oxidation of reduced iodine to iodate by either O_2 or even more oxidizing species such as H_2O_2 are not feasible, requiring prohibitively long time scales. Truesdale et al., (2001) have suggested biological mediation, facilitated by ammonia oxidizing bacteria. We also favor such reaction schemes, as during lake mixing there was a net production of iodate in the depth profile, particularly in the previously anoxic zone. This cannot be a photolytic process due, firstly, to the very chromophoric nature of the humic water which does not allow much light penetration below about 1 m, and secondly to covering of the lake in ice and snow during the winter. Substantially more work needs to be done on biological iodine transformations in fresh water ecosystems before a more certain pathway can be suggested. Iodate reduction in the hypolimnion was associated with low oxygen conditions and as such reduction by reduced species such as H_2S are feasible (Jia-Zhong and Whitfield, 1986). Reduction by microbiology is also feasible, for example, transferring from nitrate to iodate as an electron acceptor.

One of the clearest features in the Mummelsee's iodine cycle is the release of iodide during anoxic conditions in the hypolimnion. The flux was derived from the sediments and is thought to be associated with decomposition of detritus. There was also a very clear distinction between the epi- and hypolimnion based on iodide levels and particularly I^-/IO_3^- ratios. Fluxes of iodide from the sediments were estimated to range between a maximum of $1.28 \mu\text{g m}^{-2} \text{day}^{-1}$ and minimum of minus $1.98 \mu\text{g m}^{-2} \text{day}^{-1}$. The negative flux occurred in the October-November interval and is thought to be a result of major lake mortalities with the oncoming winter and subsequent scavenging of iodide to the sediments.

Interestingly, organo-I was also the dominant fraction in the spring inflow, with iodate being the next most abundant species. Iodide concentrations were low, but increased slightly throughout the year until late autumn (Figure 11). Overall iodine appears to be controlled by organic matter in the aqueous terrestrial environment, but there also remain many factors that are unknown, particularly the actual species of organic iodine and the mechanism for iodination. Moreover, more specific reaction mechanisms need to be elucidated by laboratory studies.

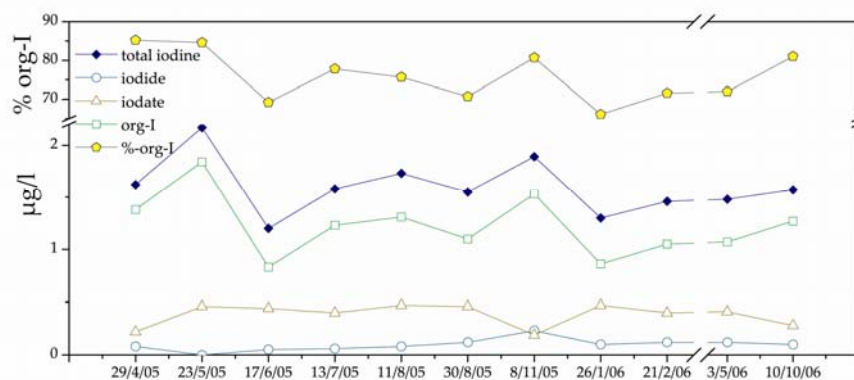


Figure 11: Iodine speciation in the spring inflow.

1.4 Conclusions

Iodine is a vital nutritional element for all mammals, including humans and also plays an important role in the atmosphere by catalytic ozone destruction and aerosol nucleation in the troposphere. In this thesis I have investigated iodine cycling in specific aqueous phase compartments: aerosols, precipitation, lakes, and springs. Some important and interesting results have been found, namely that organically bound iodine is the dominant fraction in aerosols and precipitation rather than iodine oxides such as iodate. Interestingly, unidentified, presumably anionic organic species were found in aerosols, rain and snow providing a direct observation of organic iodine. I have also shown some of the first results of organic iodine concentrations and cycling in limnic and shallow groundwater environments, in addition to the inorganic species cycling. Such processes appear to control iodine behavior in the natural environment. However, there remain many uncertainties in all compartments that remain to be elucidated, in particular:

- What is the iodine species condensing from the gas phase? Is it iodine oxides as currently believed or an organic species?
- How is iodine attached to organic matter, when is it bound (e.g. gas phase or aqueous phase) and if iodine is taken up as an oxide how is it reduced to iodide or reactive nucleophilic species such as HOI?
- What are the organic iodine species, both those observed in chromatograms, and that calculated by total iodine minus inorganic iodine?
- How is iodide maintained at observable levels in aerosols and precipitation despite theoretically very fast oxidation kinetics?
- How large is the global flux of iodine-derived aerosols? Is this important for the global radiation budget?
- How does organic iodine affect the flux of iodine from aerosols back into the gas phase and what does this imply for transport to the continents?

- What are the organic species in the Mummelsee and spring flow, how and where are they formed (e.g. soils, groundwater or in the lake)?
- How do organisms, and particularly microorganisms such as bacteria, effect iodine cycling and speciation, particularly iodination of organic matter and oxidation of iodide?
- How has iodine's flux to the sediments changed through time and how does climate affect this flux? Can iodine be used as a climate proxy?
- What new methods will be necessary to fulfill the questions raised above?

It is expected that, with the current interest in iodine chemistry, these and many other pressing questions will become clearer in the near future.

1.5 References

- Alicke, B., Hebestreit, K., Stutz, U. and Platt, U.: Iodine oxide in the marine boundary layer, *Nature*, 397, 572-573, 1999.
- Allan, B.J., McFiggans, G. and Plane, J.M.C.: Observations of iodide monoxide in the remote marine boundary layer, *Journal of Geophysical Research*, 105, 14363, 2000.
- Andersen, S., Petersen, S.B. and Laurberg, P.: Iodine in drinking water in Denmark bound in humic substances, *European Journal of Endocrinology*, 147, 663-670, 2002.
- Andersson, M., de Benoist, B., Darnton-Hill, I. and Delange, F., Iodine deficiency in Europe : a continuing public health problem. World Health Organization, Geneva (2007), pp. 1-86.
- Asplund, G. and Grimvall, A.: Organohalogenes in nature: More widely spread than previously thought, *Environmental Science and Technology*, 25, 1346-1350, 1991.
- Atarashi-Andoh, M., Schnabel, C., Cook, G., MacKenzie, A.B., Dougans, A., Ellam, R.M., Freeman, S., Maden, C., Olive, V., Synal, H.A. and Xu, S.: $^{129}\text{I}/^{127}\text{I}$ ratios in surface waters of the English Lake District, *Applied Geochemistry*, 22, 628-636, 2007.
- Baker, A.R.: Marine aerosol iodine chemistry: the importance of soluble organic iodine, *Environmental Chemistry*, 2, 295-298, 2005.
- Baker, A.R., Tunnicliffe, C. and Jickells, T.D.: Iodine speciation and deposition fluxes from the marine atmosphere, *Journal of Geophysical Research*, 106, 28743-28749, 2001.
- Biester, H., Keppler, F., Putschew, A., Martinez-Cortizas, A. and Petri, M.: Halogen Retention, Organohalogenes and the Role of Organic Matter Decomposition on Halogen Enrichment in Two Chilean Peat bogs, *Environmental Science and Technology*, 38, 1984 - 1991, 2004.
- Biester, H., Selimovic, D., Hemmerich, S. and Petri, M.: Halogens in pore water of peat bogs - the role of peat decomposition and dissolved organic matter, *Biogeosciences*, 3, 53-64, 2006.
- Bigg, E.K.: Source, nature and influence on climate of marine airborne particles, *Environmental Chemistry*, 4, 155-161, 2007.
- Bigg, E.K. and Turvey, D.E.: Source of atmospheric particles over Australia, *Atmospheric Environment*, 12, 1643-1655, 1978.
- Bloss, W.J., Lee, J.D., Johnson, G.P., Sommariva, R., Heard, D.E., Saiz-Lopez, A., Plane, J.M.C., McFiggans, G., Coe, H., Flynn, M., Williams, P.I., Rickard, A.R. and Fleming, Z.L.: Impact of halogen monoxide chemistry upon boundary layer OH and HO₂ concentrations at a coastal site, *Geophysical Research Letters*, 32, L06814, doi: 06810.01029/02004GL022084, 2005.
- Bösch, H., Camy-Peyret, C., Chipperfield, M.P., Fitzenberger, R., Harder, H., Platt, U. and Pfeilsticker, K.: Upper limits of stratospheric IO and OIO inferred from center-to-limb-darkening-corrected balloon-borne solar occultation visible spectra: Implications for total gaseous iodine and stratospheric ozone, *Journal of Geophysical Research*, 108, ACH-9, doi: 10.1029/2002JD003078, 2003.
- Broadbent, A.D. and Jones, G.B.: DMS and DMSP in mucus ropes, coral mucus, surface films and sediment pore waters from coral reefs in the Great Barrier Reef, *Marine and Freshwater Research*, 55, 849-855, 2004.
- Butler, E.C.V., Smith, J.D. and Fisher, N.S.: Influence of phytoplankton on iodine speciation in seawater, *Limnology and Oceanography*, 26, 382-386, 1981.
- Cainey, J.M.: Understanding the origin of clouds, *Environmental Chemistry*, 4, 141-142, 2007.
- Cainey, J.M., Keywood, M., Bigg, E.K., Grose, M.R., Gillett, R.W. and Meyer, M.: Flux chamber study of particle formation from *Durvillaea potatorum*, *Environmental Chemistry*, 4, 151-154, 2007a.
- Cainey, J.M., Keywood, M., Grose, M.R., Krummel, P., Galbally, I.E., Johnston, P., Gillett, R.W., Meyer, M., Fraser, P., Steele, P., Harvey, M., Kreher, K., Stein, T., Orahim, O., Ristovski, Z.D., Johnson, G., Fletcher, C.A., Bigg, E.K. and Gras, J.L.: Precursors to particles (P2P) at Cape Grim 2006: campaign overview, *Environmental Chemistry*, 4, 143-150, doi: 110.1071/EN07041, 2007b.

- Campos, M.L.A.M.: New approach to evaluating dissolved iodine speciation in natural waters using cathodic stripping voltammetry and a storage study for preserving iodine species, *Marine Chemistry*, 57, 107-117, 1997.
- Campos, M.L.A.M., Nightingale, P.D. and Jickells, T.D.: A comparison of methyl iodide emissions from seawater and wet depositional fluxes of iodine over the southern North Sea, *Tellus*, 48B, 106-114, 1996.
- Carpenter, L.J.: Iodine in the marine boundary layer, *Chemical Reviews*, 103, 4953-4962, 2003.
- Carpenter, L.J., Liss, P.S. and Penkett, S.A.: Marine organohalogens in the atmosphere over the Atlantic and Southern oceans, *Journal of Geophysical Research*, 108, 4256, doi:4210.1029/2002JD002769, 2003.
- Carpenter, L.J., Sturges, W.T., Penkett, S.A. and Liss, P.S.: Short-lived alkyl iodides and bromides at Mace Head, Ireland: Links to biogenic sources and halogen oxide production, *Journal of Geophysical Research*, 104, 1679-1689, 1999.
- Chance, R., Malin, G., Jickells, T.D. and Baker, A.R.: Reduction of iodate to iodide by cold water diatom cultures, *Marine Chemistry*, 105, 169-180, 2007.
- Charlson, R.J., Lovelock, J., Andreae, M.O. and Warren, S.G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, *Nature*, 326, 655 - 661, 1987.
- Chin, W.-C., Orellana, M.V. and Verdugo, P.: Spontaneous assembly of marine dissolved organic matter into polymer gels, *Nature*, 391, 568-572, 1998.
- Clayton, C.A., Hines, J.W. and Elkins, P.D.: Detection limits with specified assurance probabilities, *Analytical Chemistry*, 59, 2506-2614, 1987.
- Cook, P.L.M., Carpenter, P.D. and Butler, E.C.V.: Speciation of dissolved iodine in the waters of a humic-rich estuary, *Marine Chemistry*, 69, 179-192, 2000.
- Cox, R.A. and Coker, G.B.: Absorption cross section and kinetics of IO in the photolysis of CH₃I in the presence of ozone, *Journal of Physical Chemistry*, 87, 4478-4484, 1983.
- de Benoist, B., Andersson, A., Egli, I., Takkouche, B. and Allen, H., Iodine status worldwide. World Health Organization, Geneva (2004), pp. 1-46.
- DIN 32645, *Chemische Analytik– Nachweis-, Erfassungs- und Bestimmungsgrenzen*. Beuth, Berlin (1994).
- Duce, R.A., Wasson, J.T., Winchester, J.W. and Burns, F.: Atmospheric iodine, bromine, and chlorine, *Journal of Geophysical Research*, 68, 3943-3947, 1963.
- Duce, R.A., Winchester, J.W. and Van Nahl, T.W.: Iodine, bromine, and chlorine in the Hawaiian marine atmosphere, *Journal of Geophysical Research*, 70, 1775-1799, 1965.
- Duce, R.A. and Woodcock, A.H.: Difference in chemical of atmospheric sea salt particles produced in the surf zone and on the open sea in Hawaii, *Tellus*, XXIII, 427-434, 1971.
- Duce, R.A., Woodcock, A.H. and Moyers, J.L.: Variation of ion ratios with size among particles in tropical oceanic air, *Tellus*, XIX, 369-379, 1967.
- Elderfield, H. and Truesdale, V.W.: On the biophilic nature of iodine in seawater, *Earth and Planetary Science Letters*, 50, 105-114, 1980.
- Frieß, U., Wagener, T., Pundt, I., Pfeilsticker, K. and Platt, U.: Spectroscopic measurements of tropospheric iodine oxide at Neumayer station, Antarctica, *Geophysical Research Letters*, 28, 1941-1944, 2001.
- Frieß, U., Hollwedel, J., König-Langlo, G., Wagner, T. and Platt, U.: Dynamics and chemistry of tropospheric bromine explosion events in the Antarctic coastal region, *Journal of Geophysical Research*, 109, D06305, doi:06310.01029/02003JD004133, 2004.
- Fuge, R., Soils and iodine deficiency. In: O. Selinus, Editor, *Essentials of medical geology: impacts of the natural environment on public health*, Elsevier academic press, Heidelberg (2005), pp. 417-433.
- Fuge, R. and Johnson, C.C.: The geochemistry of iodine - a review, *Environmental Geochemistry and Health*, 8, 31-54, 1986.
- Gilfedder, B.S., Petri, M. and Biester, H.: Iodine speciation in rain and snow: Implications for the atmospheric iodine sink, *Journal of Geophysical Research*, 112, doi:10.1029/2006JD007356, 2007a.

- Gilfedder, B.S., Lai, S., Petri, M., Biester, H. and Hoffmann, T.: Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to droplet phases, *Atmospheric Chemistry and Physics*, Submitted, 2007b.
- Gilfedder, B.S., Petri, M. and Biester, H.: Iodine and bromine speciation in snow and the effect of orographically induced precipitation, *Atmospheric Chemistry and Physics*, 7, 2661-2669, 2007c.
- Gilfedder, B.S., Petri, M. and Biester, H.: Iodine speciation and cycling in limnic systems: observations from a humic rich headwater lake (Mummelsee), *Biogeosciences*, Published on line in BGD, 2007d.
- Heumann, K.G., Gallus, S.M., Rädlinger, G. and Vogl, J.: Accurate determination of element species by on-line coupling of chromatographic systems with ICP-MS using isotope dilution technique, *Spectrochimica Acta part B*, 53, 273-287, 1998.
- Hoffmann, T., O'Dowd, C.D. and Seinfeld, J.H.: Iodine oxide homogeneous nucleation: An explanation for coastal new particle production, *Geophysical Research Letters*, 28, 1949-1952, 2001.
- Hönninger, G., Leser, H., Sebastian, O. and Platt, U.: Ground based measurements of halogen oxides at the Hudson Bay the active long-path DOAS and passive MAX-DOAS, *Geophysical Research Letters*, 31, L04111, doi: 04110.01029/02003GL018982, 2004.
- Jia-Zhong, Z. and Whitfield, M.: Kinetics of inorganic redox reactions in seawater: 1. The reduction of iodate by bisulphide, *Marine Chemistry*, 19, 121-137, 1986.
- Jickells, T.D., Boyd, S.S. and Knap, A.H.: Cycling in the Sargasso Sea and the Bermuda inshore waters, *Marine Chemistry*, 24, 61-82, 1988.
- Jones, C.E. and Carpenter, L.J.: Chemical destruction of CH₃I, C₂H₅I, 1-C₃H₇I, 2-C₃H₇I in salt water, *Geophysical Research Letters*, 34, L13804, doi:13810.11029/12007GL029775, 2007.
- Jones, G.B. and Trevena, A.: The influence of coral reefs on atmospheric dimethylsulfide over the Great Barrier Reef, Coral Reef, Gulf of Papua and Solomon and Bismarck Seas, *Marine and Freshwater Research*, 56, 85-93, 2005.
- Jones, S.D. and Truesdale, V.W.: Dissolved iodine species in a British freshwater systems, *Limnology and Oceanography*, 29, 1016-1024, 1984.
- Keppler, F., Eiden, R., Niedan, V., Pracht, J. and Schöler, H.F.: Halocarbons produced by natural oxidation processes during degradation of organic matter, *Nature*, 403, 298-301, doi:210.1038/35002055, 2000.
- Keppler, F., Biester, H., Putschew, A., Silk, P., Schöler, H.F. and Müller, G.: Organoiodine formation during humification in peatlands: a key process in terrestrial iodine cycling, *Environmental Chemistry Letters*, 1, 219-223, 2004.
- Krupp, G. and Aumann, D.C.: The origin of iodine in soil: I. Iodine in rainfall over Germany, *Chemie der Erde*, 59, 57-67, 1999.
- Kulmala, M., Korhonen, P., Napari, I., Karlsson, A., Berresheim, H. and O'Dowd, C.D.: Aerosol formation during PARFORCE: Ternary nucleation of H₂SO₄, NH₃, and H₂O, *Journal of Geophysical Research*, 107, doi: 10.1029/2001JD000900, 2002.
- Küpper, F.C., Schweigert, N., Ar Gall, E., Legendre, J.M., Vilter, H. and Kloareg, B.: Iodine uptake by Laminariales involves extracellular, haloperoxidase-mediated oxidation of iodide, *Planta*, 207, 163-171, 1998.
- Laurberg, P., Andersen, S., Petersen, I.B., Ovesen, L. and Knudsen, N.: Humic substances in drinking water and the epidemiology of thyroid disease, *BioFactors*, 19, 145-153, 2003.
- Leck, C. and Bigg, E.K.: Source and evolution of marine aerosol-A new perspective, *Geophysical Research Letters*, 32, L19803, DOI: 19810.11029/12005GL023651, 2005.
- Leck, C. and Bigg, E.K.: Comparison of sources and nature of the tropical aerosol with the summer high Arctic aerosol, *Tellus*, Online, DOI: 10.1111/j.1600-0889.2007.00315.x, 2007.
- Lovelock, J.: Gaia as seen through the atmosphere, *Atmospheric Environment*, 6, 579-580, 1972.
- Lovelock, J., *Gaia: A new look at life on Earth.*, Oxford University Press, Oxford (1979).

- Lovelock, J., Maggs, R.J. and Wade, R.J.: Halogenated Hydrocarbons in and over the Atlantic, *Nature*, 241, 194 - 196, 1973.
- Luther, G.W. and Cole, H.: Iodine speciation in Chesapeake Bay waters, *Marine Chemistry*, 24, 315-325, 1988.
- Luther, G.W., Wu, J. and Cullen, J.B., Redox chemistry of iodine in seawater: frontier molecular orbital theory considerations. In: C.P. Huang, C.R. O'Melia and J.J. Morgan, Editors, *Aquatic Chemistry: interfacial and interspecies processes*, American Chemical Society, Washington DC (1995).
- Martino, M., Liss, P.S. and Plane, J.M.C.: Wavelength-dependence of the photolysis of diiodomethane in seawater, *Geophysical Research Letters*, 22, L06606, doi:06610.01029/02005GL025424, 2006.
- McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M.C., Feingold, G., Fuzzi, S., Gysel, M., Laarksonen, A., Lohmann, U., Mentel, T.F., Murphy, D.M., O'Dowd, C.D., Snider, J.R. and Weingartner, E.: The effect of physical and chemical aerosol properties on warm cloud activation, *Atmospheric Chemistry and Physics*, 6, 2593-2649, 2006.
- McFiggans, G.: Marine aerosols and iodine emissions, *Nature*, 433, E13, 2005.
- McFiggans, G., Coe, H., Burgess, R., Allan, J., Cubison, M., Alfarra, M.R., Saunders, R., Saiz-Lopez, A., Plane, J.M.C., Wevill, D.J., Carpenter, L.J., Rickard, A.R. and Monks, P.S.: Direct evidence for coastal iodine particles from *Laminaria* macroalgae - Linkage to emissions of molecular iodine, *Atmospheric Chemistry and Physics*, 4, 701-713, 2004.
- McFiggans, G., Plane, J.M.C., Allan, B.J. and Carpenter, L.J.: A modeling study of iodine chemistry in the marine boundary layer, *Journal of Geophysical Research*, 105, 14371-14385, 2000.
- Michel, A. and Villemant, B.: Determination of halogens (F, Cl, Br, I) sulfur and water in seventeen geological reference materials, *Geostandards Newsletter*, 27, 163-171, 2003.
- Michel, R., Ernst, T.H., Jakob, D., Klipsch, K., Szidat, S., Synal, H.A. and Schnabel, C., Long-lived radionuclides in the environment: The case of iodine-129. *EUROSAFE*, http://www.eurosafe-forum.org/products/data/5/pe_235_24_1_euro2_4_2_iodine129.pdf?PHPSESSID=933dfc3de630a555e394b81657d2af29, Berlin (2002).
- Miyake, Y. and Tsunogai, S.: Evaporation of iodine from the ocean, *Journal of Geophysical Research*, 68, 3989-3994, 1963.
- Moran, J.E., Oktay, S. and Santschi, P.H.: Sources of iodine and iodine 129 in rivers, *Water Resources Research*, 38, 24-21 to 24-10, 2002a.
- Moran, J.E., Oktay, S., Santschi, P.H. and Schink, D.R.: Atmospheric dispersal of ¹²⁹I from nuclear reprocessing facilities, *Environmental Science and Technology*, 33, 2536-2542, 1999.
- Moran, J.E., Oktay, S.D. and Santschi, P.H.: Sources of iodine and iodine 129 in rivers, *Water Resources Research*, 38, 24-21 to 24-10, 2002b.
- Moulin, V., Reiller, P., Amekraz, B. and Moulin, C.: Direct characterization of iodine covalently bound to fulvic acids by electrospray mass spectrometry, *Rapid Communications in Mass Spectrometry*, 15, 2488-2496, 2001.
- Moyers, J.L. and Duce, R.A.: Gaseous and particulate iodine in the marine atmosphere, *Journal of Geophysical Research*, 77, 5229-5238, 1972.
- Muramatsu, Y. and Wedepohl, K.H.: The distribution of iodine in the earth's crust, *Chemical Geology*, 147, 201-216, 1998.
- Murphy, D.M., Cziczo, D.J., Hudson, P.K. and Thompson, D.S.: Carbonaceous material in aerosol particles in the lower stratosphere and tropopause region, *Journal of Geophysical Research*, 112, DO4203; DOI: 4210.1029/2006JD007297, 2007.
- Müller, G., Nkusi, G. and Schöler, H.F.: Natural organohalogenes in sediments, *Journal für Praktische Chemie Chemiker-Zeitung*, 338, 23-29, 1996.
- Müller, G.: Sense or no-sense of the sum parameter for water soluble 'adsorbable organic halogens' (AOX) and 'absorbed organic halogens' (AOX-S18) for the assessment of organohalogenes in sludges and sediments, *Chemosphere*, 52, 371-379, 2003.

- Neal, C., Neal, M., Wickham, H., Hill, L. and Harman, S.: Dissolved iodine in rainfall, cloud, stream and groundwater in the Plynlimon area of mid-Wales, *Hydrology and Earth System Sciences*, 11, 283-293, 2007.
- Neal, C., Smith, C.J., Walls, J., Billingham, P., Hill, S. and Neal, M.: Comments on the hydrochemical regulation of the halogen elements in rainfall, stemflow, throughfall, and stream waters at an acidic forested area in Mid-Wales, *The Science of the Total Environment*, 91, 1-11, 1990.
- Neal, C. and Truesdale, V.W.: The sorption of iodate and iodide by riverine sediments: its implications to dilution gauging and hydrochemistry of iodine, *Journal of Hydrology*, 31, 281-291, 1976.
- O'Dowd, C.D. and Hoffmann, T.: Coastal new particle formation: a review of the current state-of-the-art, *Environmental Chemistry*, 2, 245-255, 2005.
- O'Dowd, C.D., Jimenez, J.L., Bahreini, R., Flagan, R.C., Seinfeld, J.H., Hameri, K., Pirjola, L., Kulmala, M., Jennings, S.G. and Hoffmann, T.: Marine aerosol formation from biogenic iodine emissions, *Nature*, 417, 632-636, 2002.
- O'Dowd, C.D., Facchini, M.C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y.J. and Putaud, J.P.: Biogenically driven organic contribution to marine aerosol, *Nature*, 431, 676, 2004.
- Oktyay, S., Santschi, P.H., Moran, J.E. and Sharma, P.: ^{129}I and ^{127}I transport in the Mississippi River, *Environmental Science and Technology*, 35, 4470-4476, 2001.
- Palmer, C.J., Anders, T.L., Carpenter, L.J., Küpper, F.C. and McFiggans, G.: Iodine and halocarbon response of *Laminaria digitata* to oxidative stress and links to atmospheric new particle production, *Environmental Chemistry*, 2, 282-290, 2005.
- Pechtl, S., Lovejoy, E.R., Burkholder, J.B. and von Glasow, R.: Modeling the possible role of iodine oxides in atmospheric new particle formation, *Atmospheric Chemistry and Physics*, 6, 505-523, 2006.
- Pechtl, S., Schmitz, G. and von Glasow, R.: Modelling iodide – iodate speciation in atmospheric aerosol: Contributions of inorganic and organic iodine chemistry, *Atmospheric Chemistry and Physics*, 7, 1381–1393, 2007.
- Pennington, W.: Seston and sediment formation in five Lake District lakes, *Journal of Ecology*, 62, 215-251, 1974.
- Peters, C., Pechtl, S., Stutz, J., Hebestreit, K., Hönninger, G., Heumann, K.G., Schwartz, A., Winterlik, J. and Platt, U.: Reactive and organic halogen species in three different European coastal environments, *Atmospheric Chemistry and Physics*, 5, 3357-3375, 2005.
- Plewa, M.j., Wagner, E.D., Richardson, S.D., Thurston, A.D., Woo, Y. and Mckague, A.B.: Chemical and biological characterization of newly discovered iodoacid in drinking water disinfection byproducts, *Environmental Science and Technology*, 38, 4713-4722, 2004.
- Rädlinger, G. and Heumann, K.G.: Determination of halogen species of humic substances using HPLC/ICP-MS coupling, *Fresenius Journal of Analytical Chemistry*, 359, 430-433, 1997.
- Rädlinger, G. and Heumann, K.G.: Transformation of iodide in natural and wastewater systems by fixation on humic substances, *Environmental Science and Technology*, 34, 3932-3936, 2000.
- Raisback, G.M. and Yiuo, F.: ^{129}I in the oceans: origins and applications, *The Science of the Total Environment*, 237/238, 31-41, 1999.
- Ramanathan, V., Crutzen, P.J., Kiehl, J.T. and Rosenfeld, D.: Aerosols, climate and the hydrological cycle, *Science*, 294, 2119-2124, 2001.
- Reifenhäuser, C. and Heumann, K.G.: Development of a definitive method for iodine speciation in aquatic systems, *Fresenius Journal of Analytical Chemistry*, 336, 559-563, 1990.
- Reiller, P., Mercier-Bion, F., Gimenez, N., Barre, N. and Miserque, F.: Iodination of humic acid samples from different origins, *Radiochimica Acta*, 94, 739-745, 2006.
- Reithmeier, H., Lazarev, V., Rühm, W., Schwikowski, M., Gäggeler, H.W. and Nolte, E.: Estimate of European ^{129}I Releases Supported by ^{129}I Analysis in an Alpine Ice Core, *Environmental Science and Technology*, 40, 5891 -5896, 2006.

- Richter, U. and Wallace, D.: Production of methyl iodide in the tropical Atlantic Ocean, *Geophysical Research Letters*, 31, L23S03, doi:10.1029/2004GL020779, 2004.
- Rosinski, J. and Parungo, F.: Terpene-Iodine compounds as ice nuclei, *Journal of Applied Meteorology*, 5, 119–123, 1966.
- Saiz-Lopez, A., Chance, K., Liu, X., Kurosu, T.P. and Sander, S.P.: First observations of iodine oxide from space, *Geophysical Research Letters*, 34, L12812, doi: 12810.11029/12007GL030111, 2007a.
- Saiz-Lopez, A., Mahajan, A.S., Salmon, R.A., Bauguitte, S.B., Jones, A.E., Roscoe, H.K. and Plane, J.M.C.: Boundary Layer Halogens in Coastal Antarctica, *Science*, 317, 348-351, doi:310.1126/science.1141408, 2007b.
- Saiz-Lopez, A. and Plane, J.M.C.: Novel iodine chemistry in the marine boundary layer, *Geophysical Research Letters*, 31, L04112; DOI: 01029/02003GL019215, 2004.
- Santschi, P.H. and Schwehr, K.A.: $^{129}\text{I}/^{127}\text{I}$ as a new environmental tracer or geochronometer for biogeochemical or hydrodynamic processes in the hydrosphere and geosphere: the central role of organo-iodine, *Science of the Total Environment*, 321, 2004.
- Saunders, R.W. and Plane, J.M.C.: Formation pathways and composition of iodine oxide ultra-fine particles, *Environmental Chemistry*, 2, 299-303, 2005.
- Schlegel, M.L., Reiller, P., Mercier-Bion, F., Barre, N. and Moulin, V.: Molecular environment of iodine in naturally iodinated humic substances: Insights from X-ray absorption spectroscopy, *Geochimica et Cosmochimica Acta*, 70, 5536-5551, 2006.
- Schöler, H.F. and Keppler, F.: Abiotic Formation of Organohalogens in the Terrestrial Environment, *Chimia*, 57, 33-34, 2003.
- Schöler, H.F., Keppler, F., Fahimi, I.J. and Niedan, V.W.: Fluxes of trichloroacetic acid between atmosphere, biota, soil, and groundwater, *Chemosphere*, 52, 339–354, 2003.
- Schöler, H.F. and Thiemann, W.: Natural formation of trihalomethanes in the marine and terrestrial environment. In: R. Zellner, K.H. Becker, C. Zetzsch, J. Wiesner and F. Endres, Editors, *Volatile chlorinated hydrocarbons: Occurrence, fate and impact*, Gesellschaft Dt. Chemiker (2005), pp. 122-131.
- Schöler, H.F., Nkusi, G., Niedan, V.W., Müller, G. and Spitthoff, B.: Screening of organic halogens and identification of chlorinated benzoic acids in carbonaceous meteorites, *Chemosphere*, 60, 1505–1512, 2005.
- Schönhardt, A., Richter, A., Wittrock, F., Kirk, H., Oetjen, H., Roscoe, H.K. and Burrows, J.P.: Observations of iodine monoxide (IO) columns from satellite, *Atmospheric Chemistry and Physics Discussions*, 7, 12959-12999, 2007.
- Schwehr, K.A. and Santschi, P.H.: Sensitive determination of iodine species, including the organo-iodine, for freshwater and seawater samples using high performance liquid chromatography and spectrophotometric detection, *Analytica Chimica Acta*, 482, 59-71, 2003.
- Sellegrì, K., Yoon, Y.J., Jennings, S.G., O'Dowd, C.D., Pirjola, L., Cautenet, S., Chen, H. and Hoffmann, T.: Quantification of coastal new ultra-fine particles formation from *in situ* and chamber measurements during the BIOFLUX campaign, *Environmental Chemistry*, 2, 260-270, 2005.
- Slavin, G.: Derbyshire neck and iodine deficiency, *Mercian Geologist*, 16, 79-88, 2005.
- Snyder, G. and Fehn, U.: Global distribution of ^{129}I in rivers and lakes: implications for iodine cycling in surface reservoirs, *Nuclear Instruments and Methods in Physics Research B*, 223-224, 579-586, 2004.
- Sturges, W.T. and Barrie, L.A.: Chlorine, bromine and iodine in arctic aerosols, *Atmospheric Environment*, 22, 1179-1194, 1988.
- Sugawara, K. and Terada, K.: Iodine assimilation by a marine *Navicula* sp. and the production of iodate accompanied by the growth of the algae, *Information Bulletin on Planktology in Japan*, 213-218, 1967.
- Szidat, S., Schmidt, A., Handl, J., Jakob, D., Botsch, W., Michel, R., Synal, H.A., Schnabel, C., Suter, M., López-Gutiérrez, J.M. and Städe, W.: Iodine-129: sample preparation, quality control and analysis of pre-nuclear materials and of natural waters from Lower Saxony, Germany, *Nuclear Instruments and Methods in Physics Research B*, 172, 699-710, 2000.

- Tarasick, D.W. and Bottenheim, J.W.: Surface ozone depletion episodes in the Arctic and Antarctic from historical ozonesonde records, *Atmospheric Chemistry and Physics*, 2, 197–205, 2002.
- Tian, R.C. and Nicolas, E.: Iodine speciation in the northwestern Mediterranean Sea: method and vertical profile, *Marine Chemistry*, 48, 151-156, 1995.
- Truesdale, V.W. and Jones, S.D.: The variation of iodate and total iodine in some UK rainwater samples during 1980-1981, *Journal of Hydrology*, 179, 67-86, 1996.
- Truesdale, V.W., Kennedy, H., Agusti, S. and Waite, T.J.: On the relative constancy of iodate and total-iodine concentrations accompanying phytoplankton blooms initiated in mesocosm experiments in Antarctica, *Limnology and Oceanography*, 1569–1574, 2003.
- Truesdale, V.W. and Spencer, C.P.: Studies on the determination of inorganic iodine in seawater, *Marine Chemistry*, 2, 33-47, 1974.
- Truesdale, V.W., Watts, S.F. and Rendell, A.R.: On the possibility of iodide oxidation in the near surface of the Black Sea and its implications to iodine in general oceans, *Deep-Sea Research*, 48, 2397-2412, 2001.
- Ullman, W.J. and Aller, R.C.: Dissolved iodine flux from estuarine sediments and implications for the enrichment of iodine at the sediment water interface, *Geochimica et Cosmochimica Acta*, 44, 1177-1184, 1980.
- Väkevä, M., Hämeri, K. and Aalto, P.P.: Hygroscopic properties of nucleation mode and Aitken mode particles during nucleation bursts and in background air on the west coast of Ireland, *Journal of Geophysical Research*, 107, 8104, 2002.
- Vogt, R., Sander, R., von Glasow, R. and Crutzen, P.J.: Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study, *Journal of Atmospheric Chemistry*, 32, 375-395, 1999.
- von Glasow, R. and Crutzen, P.J., Tropospheric halogen chemistry. In: H.D. Holland and K.K. Turekian, Editors, *Treatise on Geochemistry*, Elsevier (2003), pp. 21-63.
- von Glasow, R. and Crutzen, P.J., Tropospheric halogen chemistry. In: H.D. Holland and K.K. Turekian, Editors, *Treatise on Geochemistry*, Elsevier (2007), pp. 21-63.
- Wada, R., Beames, J.M. and Orr-Ewing, A.J.: Measurement of IO radical concentrations in the marine boundary layer using a cavity ring-down spectrometer, *Journal of Atmospheric Chemistry*, 58, 2007.
- Whalley, L.K., Furneaux, K.L., Gravestock, T., Atkinson, H.M., Bale, C.S.E., Ingham, T., Bloss, W.J. and Heard, D.E.: Detection of iodine monoxide radicals in the marine boundary layer using laser induced fluorescence spectroscopy, *Journal of Atmospheric Chemistry*, 58, 19-39, 2007.
- Williams, J., Gros, V., Atlas, E., Maciejczyk, K., Batsaikhan, A., Schöler, H.F., Forster, C., Quack, B., Yassaa, N., Sander, R. and Van Dingenen, R.: Possible evidence for a connection between methyl iodide emissions and Saharan dust, *Journal of Geophysical Research*, 112, D07302, doi:07310.01029/02005JD006702, 2007.
- Winchester, J.W. and Duce, R.A.: The global distribution of iodine, bromine, and chlorine in marine aerosols, *Naturewissenschaften*, 54, 110-113, 1967.
- Wittrock, F., Müller, R., Richter, A., Bovensmann, H. and Burrows, J.P.: Measurements of Iodine monoxide (IO) above Spitsbergen, *Geophysical Research Letters*, 27, 1471-1474, 2000.
- Wong, G.T.F., Brewer, P.G. and Spencer, D.W.: The distribution of particulate iodine in the Atlantic Ocean, *Earth and Planetary Science Letters*, 32, 441-450, 1976.
- Wong, G.T.F. and Cheng, X.H.: Dissolved organic iodine in marine waters: determination, occurrence and analytical implications, *Marine Chemistry*, 59, 271-281, 1998.
- Wong, G.T.F., Piumsomboon, A.U. and Dunstan, W.M.: The transformation of iodate to iodide in marine phytoplankton cultures, *MARINE ECOLOGY PROGRESS SERIES*, 237, 27–39, 2002.
- Woodcock, A.H., Duce, R.A. and Moyers, J.L.: Salt particles and raindrops in Hawaii, *Journal of the Atmospheric Sciences*, 28, 1252-1257, 1971.

- Wuilloud, R.G., de Wuilloud, J.C.A., Vonderheide, A.P. and Caruso, J.A.: Determination of iodinated phenol species at parts-per-trillion concentration levels in different water samples by solid-phase microextraction/offline GC-ICP-MS, *Journal of Analytical Atomic Spectroscopy*, 18, 1119-1124, 2003.
- Yoon, Y.J., Lee, B.Y., Choi, T.J., Seo, T.G. and Yum, S.S., Austral summer particle formation events observed at the King Sejong station. In: C.D. O'Dowd and P.E. Wagner, Editors, *Nucleation and Atmospheric Aerosols (ICNAA) 17th international conference*, Springer, Galway, Ireland (2007).
- Zingler, J. and Platt, U.: Iodine oxide in the Dead Sea Valley: Evidence for inorganic sources of boundary layer IO, *Journal of Geophysical Research*, 110, D07307, doi:07310.01029/02004JD004993, 2005.

Chapter 2:

Atmosphere

2.1 Iodine speciation in rain and snow: Implications for the atmospheric iodine sink

B. S. Gilfedder¹, M. Petri² and H. Biester¹

1. *Institut für Umweltgeochemie, Neuenheimer Feld 236 69120 Heidelberg Germany*

2. *Bodensee-Wasserversorgung, Sipplingen Laboratory Germany*

Status: published *Journal of Geophysical research: Atmospheres*

Abstract:

Atmospheric iodine models currently predict iodate as the only stable iodine sink species in the troposphere. However, it is shown here using IC-ICP-MS that iodate is the least abundant iodine species in precipitation (rain and snow) collected from various locations in southern Germany, the Swiss Alps and Patagonia (Chile). The majority of iodine is associated with organic compounds (av. 56 %) followed by iodide (av. 27 %). Although the exact structure of the organic fraction remains ambiguous and is probably of higher molecular weight, a smaller portion of the iodo-organic compounds are anionic (5-20% of total I). One of these anionic organo-I peaks is present in all rain and most snow chromatograms and is generally responsible for 5-18% of total iodine. This suggests a ubiquitous atmospheric iodine species. The data indicate that organic iodine compounds play an important role in the global atmospheric iodine cycle and the atmospheric iodine sink. As such, future tropospheric iodine models must consider organic-I reactions.

2.1.1 Introduction

Iodine is involved in a number of important tropospheric cycles. In particular, ozone destruction and cloud condensation nuclei formation (and perhaps therefore an influence on the earth's albedo) are significant aspects of atmospheric iodine chemistry [O'Dowd *et al.*, 2002b; von Glasow and Crutzen, 2003]. Gas phase iodine species [e.g. CH₃I, CH₂I₂, C₂H₂I, CH₂ClI and I₂; Aliche *et al.*, 1999; McFiggans *et al.*, 2000 McFiggans, 2005] and source strengths of iodine emitted from the ocean have been rather extensively researched since the pioneering work of Lovelock *et al.*, [1973], although the global iodine flux (ca. 250-400 Ggyr⁻¹) is still poorly constrained [Orlando, 2003]. So far, it has been shown that these simple organo-halogens and I₂ are rapidly photolysed in the atmosphere to I⁰, whereafter I⁰ can cycle through a multitude of short lived highly reactive species including IO, OIO, HOI, IBr, HI, and I₂O₂ [see von Glasow and Crutzen, 2003 for a concise review]. These species are thought to form iodine oxide aerosols (I₂O₅; Saunders and Plane, [2005]) as the final iodine sink species; although Baker, [2005] has shown in two cruises of the northern and southern hemispheres that a significant proportion of marine aerosol iodine is either iodide or organically bound. While it is well known that wet and dry deposition are the terminal sinks for atmospheric iodine [Vogt *et al.*, 1999], there is very little field data on iodine speciation in rainfall or aerosols. Moreover, most of the research to date is theoretical and

calculated through models with many inherent assumptions that may or may not be applicable. Aside from the interest in atmospheric chemistry, rainfall is thought to be one of the major contributors (the other is rock weathering; *Moran et al.*, 2002) to terrestrial iodine levels and may therefore be a direct influence on the prevalence of iodine deficiency disorders. As such, our aim with this communication is to shed some light on the final atmospheric iodine sink by analysing iodine speciation in precipitation. To the best of our knowledge this is the first report of iodine speciation, including the organically bound fraction, in rain and snow from a continental interior. It also presents the first ‘hints’ as to the nature of the organically bound iodine in rainfall.

2.1.2 Methods:

The majority of precipitation samples were collected periodically (March 2005 to February, 2006) on the roof of the *Bodensee Wasserversorgung* laboratory located on the shore of the Überlinger See, Lake Constance, Germany (Figure 1). For monthly samples at Lake Constance a glass funnel, packed with a small amount of quartz wool, was placed into a 1 l LDPE bottle, and secured on the laboratory roof. For samples taken over a 24h period or less no quartz wool was used. No distinction was made between wet and dry deposition and we assume the results are the sum of both. One-off rain samples were also taken from the Alps (Sedrun), a small lake in the northern Black Forest (Mummelsee), both locations >1000m a.s.l, and ‘SKY’ and ‘GC1’ peat bogs in Patagonia, Chile, from *Biester et al.*, [2003]. Fresh and aged snow was sampled from various sites around Lake Constance whereas only fresh snow was collected from the Mummelsee. In addition, glacier ice samples (gratefully donated by Dr. Margit Schwikowski) from the Fiescherhorn glacier (3900m asl dated 1947-1969 [*Jenk et al.*, 2004; *Jenk et al.*, 2002]) were also analysed.

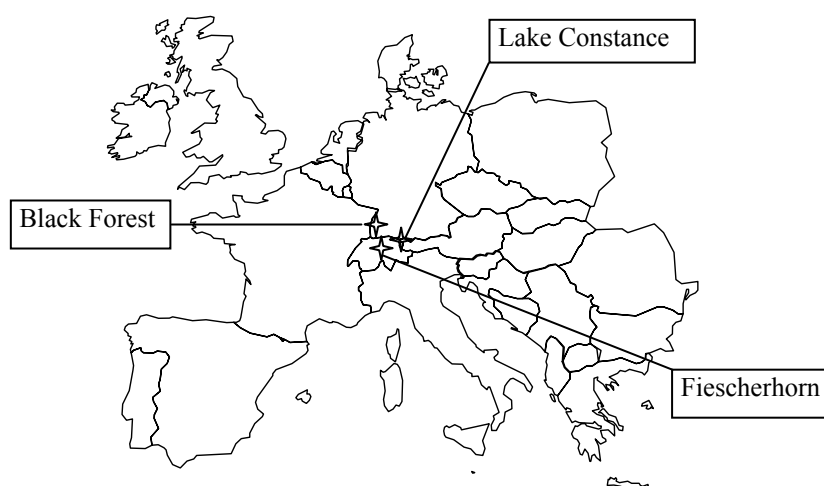


Figure 1: Primary rain, snow and glacier sample locations.

All samples were filtered through rinsed 0.45 μm cellulose acetate filters after a small amount of sample was first filtered and discarded. Samples were then refrigerated at 4°C until analysed [usually within 4 days but in some instances within 1 month; *Campos*, 1997]. Samples taken over a 24h period or less were analysed on the day of collection. While no sterilizing agents were added

to the sample bottles, the organically bound iodine content of samples taken and analysed over a 24h period or less showed no significant differences to those sampled over longer time frames. As such, we do not consider that post-depositional changes have significantly affected our results. Total iodine and bromine concentrations were measured by inductively coupled plasma-mass spectroscopy (ICP-MS). Iodine and bromine species (iodide, iodate, bromide, bromate and organically bound I/Br) were quantified by coupling an ion chromatograph to the ICP-MS (IC-ICP-MS). Iodine and bromine species were quantified using a Dionex AS16 column with an AG16 guard column, 35 mmol NaOH eluent, a flow rate of 0.9 mlmin⁻¹, a syringe flush volume of 1 ml between samples, and cyclone spray chamber on a Perkin Elmer quadrupole ICP-MS. This method has a detection limit for aqueous iodine species of about 0.2 nmol/l. Memory effects were evaluated by periodically running blank samples between regular samples. All iodine species in blanks were consistently below detection limits. Organically bound iodine was calculated as total iodine minus the inorganic iodine species. Often unidentified organic iodine species were observed in the chromatograms; while not strictly correct these species have been quantified based on the iodide calibration curve. This should not pose a large problem as all iodine is converted to I⁺ in the plasma prior to quantification with the mass spectrometer. Sodium was analysed when enough sample material was available with a Perkin Elmer flame AAS after acidification with HNO₃.

2.1.3 Results

2.1.3.1 Total iodine concentrations and its terrestrial distribution

Total iodine concentrations in rainfall at Lake Constance 2005 averaged 11.4 ± 6.7 nmolL⁻¹ (Figure 2). The rain samples from the Alps and the Black Forest contained 10.1 nmolL⁻¹ and 14 nmolL⁻¹ total iodine respectively. It is difficult to compare total iodine concentrations with many past works, for example *Campos et al.*, [1996] and *Baker et al.*, [2001], as these studies do not quantify the organic fraction, assuming that total iodine is the sum of the inorganic species I⁻ and IO₃⁻. Indeed, on comparing the average Σ inorganic iodine concentration (6.8 nmolL⁻¹) from *Campos et al.*, [1996] against our total iodine levels we note that their iodine levels are comparatively low. ICP-MS data from *Moran et al.*, [1999], sampling a wide area of the United States, and *Michel et al.*, [2005] from northern Germany found similar iodine concentrations (average 13.4 and 10.8 nmolL⁻¹ respectively) to our results. Our values are slightly lower than neutron activation analysis results (av. 17.3 ± 6.3 nmolL⁻¹) given for a nearby site in *Krupp and Aumann*, [1999].

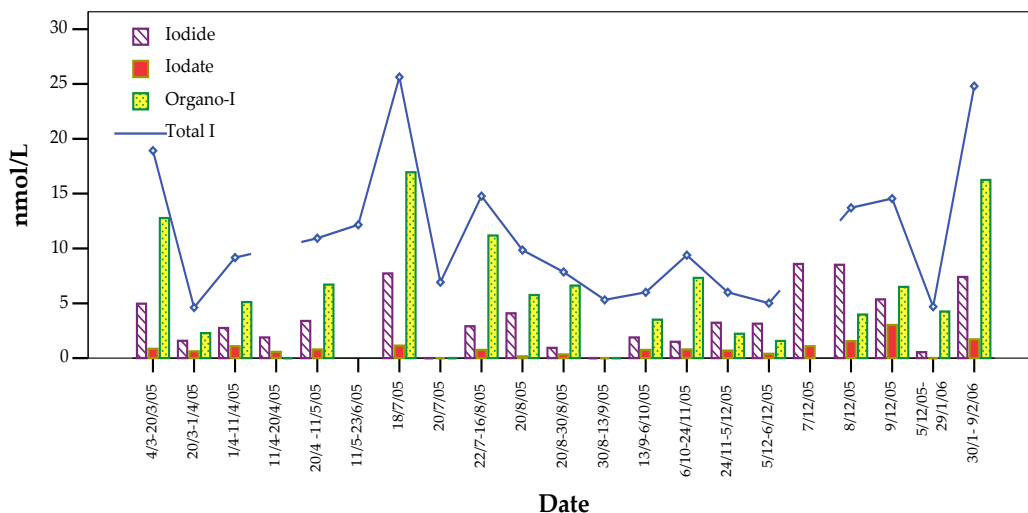


Figure 2: Total iodine, I^- , IO_3^- and organically bound iodine in rain samples from Lake Constance. Where no data exists no analysis was made.

It appears that total iodine concentrations slightly increase over the summer months (Figure 2); however, the varying sample dates make it difficult to ascertain a clear pattern. *Campos et al.*, [1996] also suggest an increase of iodine concentrations over summer, while *Truesdale and Jones*, [1996] and *Baker et al.*, [2001] note no relationship between iodine concentrations in rain and season. Thus, a seasonal variation in atmospheric iodine levels, as represented by rainfall, remains uncertain. The highest iodine concentration was associated with a summer electrical storm, which was followed by substantially lower iodine concentrations two days later. The storm rainfall also displayed the highest concentration of organically bound iodine and was the only rain sample to contain bromate (7.9 nmolL^{-1} ; supporting information Table 1) and either iodoacetic acid or iodopropionic acid. We also note bromate in some aged snow samples which may be related to extended exposure to sunlight, however there is insufficient data to make any firm assessment (Supplementary Material Table 1).

Table 1: Averages and ranges (brackets) for total iodine, iodide, iodate, organically bound iodine (nmolL^{-1}), and iodide/iodate ratios in rain and snow samples.

Sample site	Total I	I^-	IO_3^-	Org-I	IO_3^-/I^-
Lake Constance rain n=21	11.4 (4.7-26.2)	3.9 (0.5-8.5)	0.95 (<0.2-3)	7.15 (3.5-17)	0.24 (0.13-0.56)
Lake Constance snow n=15 [◇]	5.3 (1.6-9.8)	2.7 (0.6-4.4)	0.26 (0.3-5) [§]	2.8	0.1 [§]
Alps rain (Sedrun) n=1	10.1	4.1	0.17	5.7	0.04
Mummelsee (rain) n=1	14.03	3.31	1.94	8.75	0.6
Mummelsee (snow) n=4	14.7	6	<0.17	8.67	-
Patagonian peat bogs* n=3	4.02	2.7	<0.1	1.34	-

* Analysed with a less precise ion exchange column and a Scotts spray chamber that rendered a detection limit of 0.2 nmol/L . § Only 4 snow samples had iodate above the detection limit. ◇ old column for 8 out of the 15 samples.

Atmospheric iodine systematics in the terrestrial environment is of major importance as it is a vital element for all mammals [*Fuge and Johnson*, 1986]. Research to date, assuming the sum of inorganic iodine accounts for total iodine, suggest that iodine is not associated with oceanic

saltwater particles as no significant correlation between Na and $I_{\Sigma\text{inorganic}}$ has been found [Campos *et al.*, 1996]. However, by using ICP-MS to unequivocally determine total iodine concentrations we have found highly significant correlations (Figure 3b; $r^2=0.67$, $p<0.001$) between Na and total iodine and also between total iodine and total bromine in rain and snow from Lake Constance, the Black Forest and ice samples from the Fiescherhorn glacier ($r^2=0.82$, Figure 3a). Moreover, when we sum the inorganic iodine and assume this is total iodine, as conducted in previous studies, no relationships are observed (I:Br $r^2=0.22$, I:Na $r^2=0.03$, data not shown). This suggests that previous methods do not capture the total iodine flux and hence significant relationships may be obscured. The correlations observed here is most likely the result of common scavenging mechanisms during precipitation.

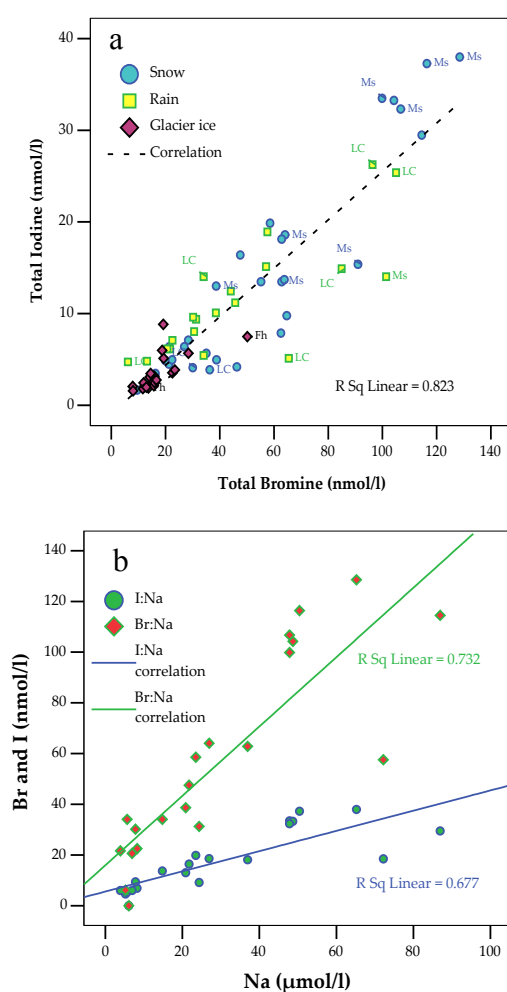


Figure 3: a) Correlation between total iodine and bromine in rain, snow and glacier samples from Lake Constance (LC), the northern Black Forest (Ms) and the Fiescherhorn glacier, Switzerland (Fh). b) Correlation between Br and I to Na: snow samples from the Black Forest and rain samples from Lake Constance.

In contrast to chlorine, which is derived from direct transfer of seawater directly to the atmosphere with little or no fractionation, iodine is highly enriched (relative to seawater) in precipitation from Lake Constance and the Black Forest. Enrichment factors for iodine in rainfall (defined as molar I:Na ratio in rain/I:Na ratio in seawater, given hereafter as EF_{NaI}), at Lake Constance range from

280 to ~ 2100 with an average of 970. Snow data from the Black Forest indicates that the enrichment of iodine in snow is lower (average = 200) than the iodine enrichment in rain, although this is a small dataset and is confined to one sampling campaign (n=11). This relatively small dataset can be significantly increased if, instead of EF_{NaI} ratios, we consider EF_{BrI} ratios. This is valid due to the very little enrichment or depletion of Br (compared to that of iodine) in rainfall and snow compared the ocean. EF_{BrI} data show much the same trend as Br_{NaI} with average iodine enrichments in rain and snow from Lake Constance of 566 and 350 respectively. Enrichment of iodine using EF_{BrI} in the glacial samples shows a virtually identical enrichment factor to that observed in snow samples from Lake Constance with an average EF of 370. These high values are not unexpected and are very similar to rain and aerosol enrichment factors observed in $<1\mu\text{m}$ aerosols near and over the ocean [Baker, 2005; Baker et al., 2000; Duce et al., 1963; Duce et al., 1965; Sander et al., 2003; Woodcock et al., 1971]. Enrichment of iodine in oceanic aerosol and rain has been known for some time [Duce et al., 1965; Woodcock et al., 1971] and is thought to be a product of both; 1) condensation of gaseous iodine species produced by oxidation of biogenic iodine emissions; and 2) the bubble bursting phenomena where iodine is preferentially concentrated in ejected droplets, probably derived mostly from the oceanic surface microlayer. Aerosol iodine may also be mixed with marine salt, probably as particles grow, and is usually associated with organics [Baker, 2005; Middlebrook et al., 1998; Murphy et al., 1997; Seto and Duce, 1972]. The consistently higher enrichment factors in rain compared to snow may be related to either higher biological productivity in the ocean over summer months or exclusion of the large iodine atom from the snow crystal structure during freezing.

2.1.3.2 Iodine speciation and the atmospheric iodine sink

The atmospheric chemistry of iodine is a complicated system comprised of multiple photocatalytic cycles producing highly reactive intermediate iodine species [e.g. HOI, IO, I_2 and IBr; von Glasow and Crutzen, 2003]. While there is continuing work on the iodine flux species [McFiggans et al., 2004], there has been sparse research on the final atmospheric iodine sink and particularly the speciation of iodine once it condenses from the gas phase to aerosol or diffuses into aqueous droplets. The next section presents the results for iodine speciation in precipitation and gives an insight into iodine speciation in the terminal atmospheric sink.

The majority of iodine in precipitation at Lake Constance is organically bound (av. 6.3 nmolL^{-1} ; 56%), and I^- (av. 4 nmolL^{-1} ; 27%) is consistently more abundant than IO_3^- (av. 1.3 nmolL^{-1} ; ~10%) (Figure 2 and Table 1). Moreover, snow consistently displayed lower molar IO_3^-/I^- ratios than rain when iodate was detectable. A similar species distribution is observed for rain samples from the Alps, the Black Forest, and Patagonia (Table 1). For Lake Constance, there do not appear to be any

strong seasonal patterns in inorganic iodine speciation. In contrast, organically bound iodine concentrations (and percentages; see supplementary material Figure 1) are higher during the summer months than during the winter (Figure 2). This may be due to increased incoming radiation from the sun during the summer (and vice versa in the winter) leading to 1) more (or in winter, less) energy for photolytic reactions in the atmosphere; and 2) considerably higher amounts of volatile and particulate organic carbon (VOC) compounds from the ocean and forest ecosystems during the summer [Cavalli *et al.*, 2004; O'Dowd *et al.*, 2002b].

The rain speciation data, and particularly the low iodate levels, differ from tropospheric iodine speciation models, which suggest that IO_3^- (as an aerosol) is the only stable iodine sink [Chatfield and Crutzen, 1990; McFiggans *et al.*, 2000; Vogt *et al.*, 1999]. In fact, atmospheric halogen models give such a rapid oxidation rate for I^- by, for example HOCl, that I^- should theoretically be non-existent [Vogt *et al.*, 1999]. Moreover, I^- should be photolysed at the particle surface to I_2 and subsequently reenter the gas phase. The discrepancy between observed and predicted iodine speciation was also pointed out by Baker *et al.* [2001] where IO_3^-/I^- ratios measured in rainfall from a coastal site in England were significantly lower than predicted by model calculations (max. ratio of 10 for oceanic and 0.8 for continental rain). Moreover, no IO_3^- was detected in marine aerosols in the southern hemisphere during an extended cruise [Baker, 2004]; although a subsequent transect by the same author found iodate and organically bound iodine in marine aerosols from northern and southern hemispheres [Baker, 2005]. Murphy *et al.*, [1997] and Middlebrook *et al.*, [1998] have also elegantly shown, using the PALMS instrument, a strong association between iodine and organic rich particles in unpolluted aerosols of marine origin. In contrast Laniewski *et al.*, [1999] found very little iodine associated with organics in rain and snow. However, this is more likely a function of the AOX method used to isolate the organo-halogens as it was initially developed for wastewater rather than trace analytics.

The results from this study further indicate that organic iodine compounds and I^- are the most important sink for atmospheric iodine and that IO_3^- is relatively insignificant. For example, the maximum IO_3^-/I^- ratio observed at Lake Constance was 0.56 with an average of 0.24; significantly lower than the IO_3^-/I^- ratio for rain derived from European continental air masses (0.8 and 3.9 $n=2$) given in Baker *et al.*, [2001] and marine rainfall (av. ratio ~ 1 $n>100$) given by Campos *et al.*, [1996] and Truesdale and Jones, [1996]. This suggests that once I^- is formed deposition occurs before oxidation can take place or that oxidation of I^- to IO_3^- is too slow to be significant under normal atmospheric conditions. It also indicates that iodine oxide aerosols are reduced during their evolution. Iodide that is oxidized to I_2 or HOI, as per the conceptual model in von Glasow and Crutzen [2003], is likely to react with atmospheric organic compounds such as material from the

oceanic surface micro layer, terrestrial and oceanic isoprenes or terrestrially derived terpenes or their derivatives [Cavalli *et al.*, 2004; Greenberg *et al.*, 2005; Middlebrook *et al.*, 1998]. There is an increasing amount of data suggesting that such natural organic compounds play an important role in atmospheric chemistry, e.g. forming aerosols and CCN [Claeys *et al.*, 2004; Jacobson *et al.*, 2000; O'Dowd *et al.*, 2002a; O'Dowd *et al.*, 2004]. The organic iodine species may also be of marine origin, as Middlebrook *et al.* [1998] have demonstrated the existence of I-organic associations in unpolluted marine aerosols at Cape Grim, Tasmania, Australia. It was assumed that the organo-I originated from bubble bursting and subsequent ejaculation of the organic rich surface film into the atmosphere; although Baker, [2005] prefers a direct gas to particulate reaction for aerosol organo-I. Therefore, no matter the source of the organic entities, it seems likely that the highly reactive I_2 or HOI, formed by photolytically driven activation of I^- at the aerosol surface, will also react with condensed VOCs or other organic compounds to form C-I.

While the exact structure of the organo-I compounds in precipitation remains elusive, a portion of the organically bound iodine is associated with unidentified, but probably anionic (interacts with the ion exchange column's stationary phase) moieties. This can be seen as 1-5 additional peaks that consistently appear in IC-ICP-MS chromatograms of rain and snow from Lake Constance, the Alps, the Black Forest and Patagonia, Chile (Figure 4 and supporting data Figures 2-4). These peaks account for 5-20% of total iodine in rain and 5-15% of iodine in snow samples.

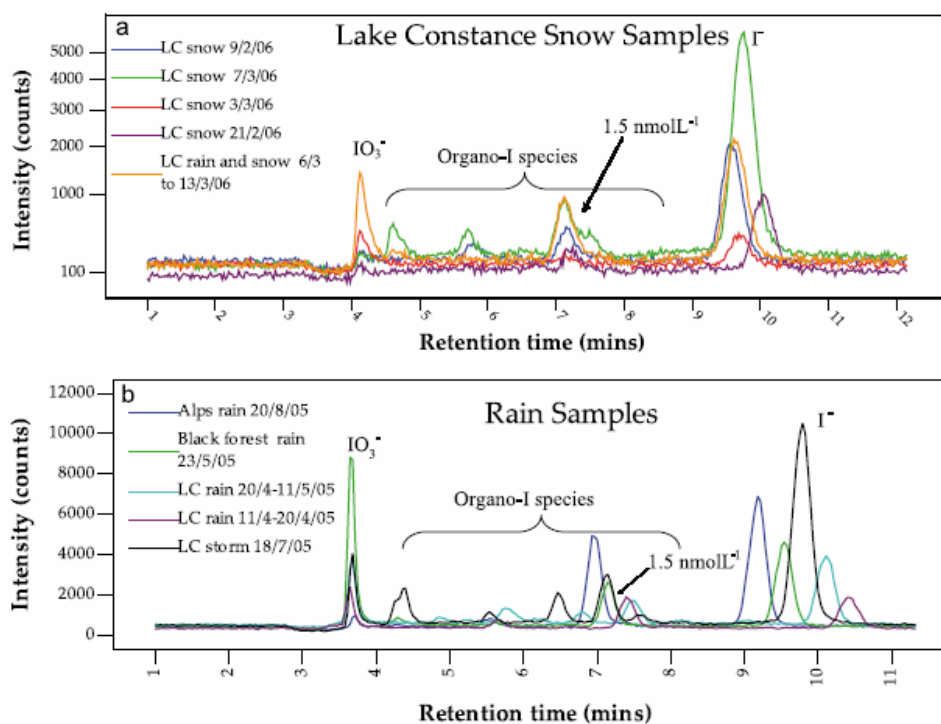


Figure 4: IC-ICP-MS chromatograms of selected snow (a) and rain (b) samples from Lake Constance, the Alps and the Black Forest. Note anionic iodine species between iodide and iodate. Shifts in the retention time are related to column age.

Two of these unidentified peaks are also observed in certain ice core samples from the Fiescherhorn glacier, Switzerland. Of particular interest, one unidentified peak between the iodate and iodide peaks (retention time 6.8-7.4 mins depending on column age) is evident in all rain, many of the snow and one of the ice core chromatograms. This peak alone usually accounts for 5-10% of total iodine in rain and snow, and on one occasion even made up 20% of the total rain iodine. This suggests a globally important iodine species. Interestingly, many of the ice core samples, although more than one year old, contained another unidentified iodine species at a shorter retention time (ca. 5.5 mins). This same peak is also seen in rain chromatograms at Lake Constance and in snow from the Black Forest. These observations indicate that organically bound iodine is able to be dispersed over a wide area by both rain and snow. Definitive identification of these compounds is hampered by the unavailability of reference materials and perhaps an unequivocal method that can characterize the other elements in the organic molecules. So far, iodoacetic acid, diiodoacetic acid, iodopropionic acid, I_3^- and a variety of aromatic iodine compounds have been tested; however none of these, as yet, correspond to the observed peaks.

2.1.4 Conclusions

Organo-I was the dominant iodine species in all precipitation samples analysed. We believe that at least one of these species is globally ubiquitous based on rain and snow samples from the Black Forest and Lake Constance (Germany), Patagonia (Chile) and the Fiescherhorn glacier (Switzerland). Moreover, in contrast to existing atmospheric iodine models iodide is considerably more abundant than iodate ($IO_3^-/I^- = 0.25$), suggesting reduction of iodate and possibly cycling between organo-I and iodide. This has some interesting implications. Firstly, reactions between IO, HOI, and I_2 and atmospheric organic matter may reduce iodine's ozone destruction potential by forming stable C-I bonds and, secondly, indicates that organic reactions must be incorporated into iodine atmospheric cycling models.

Acknowledgements

We would like to thank Dr. H. Reithmeier, Physik Department Technische Universität München and Margit Schwikowski, Laboratory for Radiochemistry and Environmental Chemistry, Paul Scherrer Institute Switzerland for the glacier samples and Professor H.F. Schöler for the diiodoacetic acid standard. BSG would also like to thank Roland von Glasow for very stimulating discussions and valuable comments on the manuscript. Two anonymous reviewers are also thanked for improvement of the manuscript. This project was funded by the Deutsche Forschungsgemeinschaft BI 734/5-1/2 to Harald Biester.

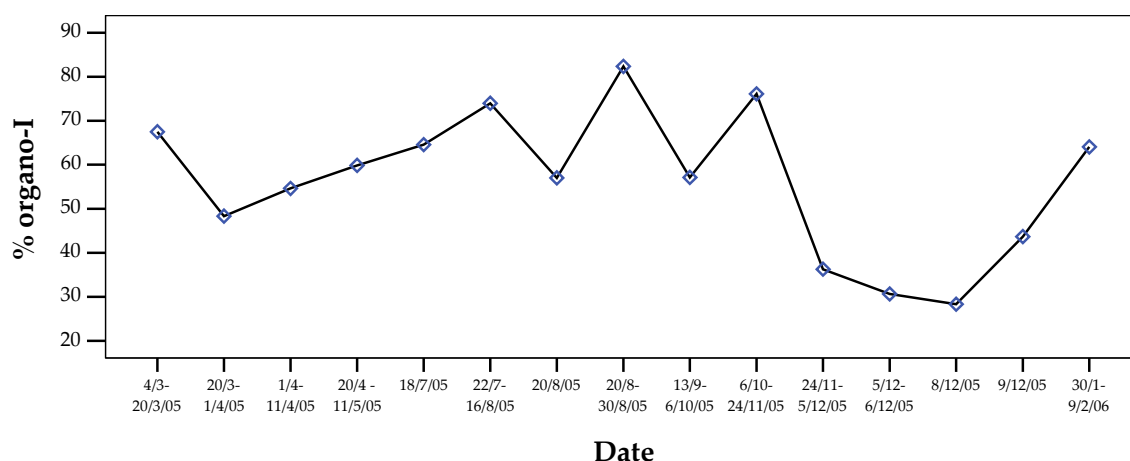
2.1.5 References

- Alicke, B., K. Hebestreit, U. Stutz, and U. Platt, Iodine oxide in the marine boundary layer, *Nature*, 397, 572-573, 1999.
- Baker, A.R., Inorganic iodine speciation in tropical Atlantic aerosol, *Geophys. Res. Lett.*, 31, L23S02, 2004.
- Baker, A.R., Marine aerosol iodine chemistry: the importance of soluble organic iodine, *Environ. Chem.*, 2, 295-298, 2005.
- Baker, A.R., D. Thompson, A.M. Campos, S.J. Parry, and T.D. Jickells, Iodine concentrations and availability in atmospheric aerosol, *Atmos. Environ.*, 34, 4331-4336, 2000.
- Baker, A.R., C. Tunnicliffe, and T.D. Jickells, Iodine speciation and deposition fluxes from the marine atmosphere, *J. Geophys. Res.*, 106, 28743-28749, 2001.
- Biester, H., F. Keppler, A. Putschew, A. Martinez-Cortizas, and M. Petri, Halogen Retention, Organohalogens and the Role of Organic Matter Decomposition on Halogen Enrichment in Two Chilean Peat bogs, *Environ. Sci. Technol.*, 38, 1984 - 1991, 2003.
- Buseck, P.R., and S.E. Schwartz, Tropospheric Aerosols, in *Treatise on Geochemistry*, edited by H.D. Holland, and K.K. Turekian, pp. 91-142, Elsevier, 2003.
- Campos, M.L.A.M., New approach to evaluating dissolved iodine speciation in natural waters using cathodic stripping voltammetry and a storage study for preserving iodine species, *Mar. Chem.*, 57, 107-117, 1997.
- Campos, M.L.A.M., P.D. Nightingale, and T.D. Jickells, A comparison of methyl iodide emissions from seawater and wet depositional fluxes of iodine over the southern North Sea, *Tellus*, 48B, 106-114, 1996.
- Cavalli, F., M.C. Facchini, S. Decesari, M. Mircea, L. Emblic, S. Fuzzi, D. Ceburnis, Y.J. Yoon, C.D. O'Dowd, J.P. Putaud, and A. Dell'Acqua, Advances in characterization of size-resolved organic matter in marine aerosol over the north Atlantic, *J. Geophys. Res.*, 109 (D24215), 1-14, 2004.
- Chatfield, R.B., and P.J. Crutzen, Are there interactions of iodine and sulfur in marine air photochemistry?, *J. Geophys. Res.*, 95 (D13), 22319-22341, 1990.
- Claeys, M., B. Graham, G. Vas, W. Wang, R. Vermeylen, V. Pashynska, J. Cafmeyer, P. Guyon, M.O. Andreae, P. Artaxo, and W. Maenhaut, Formation of Secondary organic aerosols through photooxidation of isoprene, *Nature*, 303, 1173-1176 2004.
- Dimmer, C.H., P.G. Simmonds, G. Nickless, and M.R. Nickless, Biogenic fluxes of halomethanes from Irish peatland ecosystems, *Atmos. Environ.*, 35 (2), 321-330, 2000.
- Duce, R.A., J.T. Wason, J.W. Winchester, and F. Burns, Atmospheric iodine, bromine, and chlorine, *J. Geophys. Res.*, 68 (13), 3943-3947, 1963.
- Duce, R.A., J.W. Winchester, and T.W. Van Nahl, Iodine, bromine, and chlorine in the Hawaiian marine atmosphere, *J. Geophys. Res.*, 70 (8), 1775-1799, 1965.
- Duce, R.A., A.H. Woodcock, and J.L. Moyers, Variation of ion ratios with size among particles in tropical oceanic air, *Tellus*, XIX (3), 369-379, 1967.
- Fuge, R., and C.C. Johnson, The geochemistry of iodine - a review, *Environ. Geochem. Health*, 8 (2), 31-54, 1986.
- Greenberg, J.P., A.B. Guenther, and A. Turnipseed, Marine organic halide and isoprene emissions near Mace Head, Ireland, *Environ. Chem.*, 2, 219-294, 2005.
- Jacobson, M.C., H.C. Hansson, K.J. Noon, and R.J. Charlson, Organic atmospheric aerosols: Review and state of the science, *Rev. Geophys.*, 38 (2), 267-294, 2000.
- Jenk, T., H.W. Gäggeler, A.S. Palmer, M. Schwikowski, and M. Leuenberger, Temperature reconstruction from the Fiescherhorn 2002 ice core, pp. <http://lch.web.psi.ch/pdf/anrep04/30.pdf>, PSI, Bern, 2004.
- Jenk, T., H.W. Gäggeler, A.A. Scherzman, and M. Schwikowski, Recovery of a 150m ice core down to bedrock from the Fiescherhorn Glacier, pp. <http://lch.web.psi.ch/pdf/anrep02/023-analytics.pdf>, PSI, Bern, 2002.

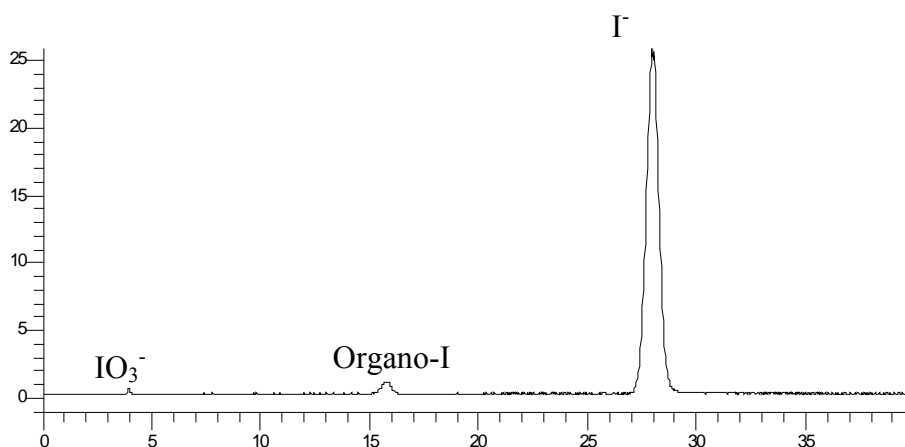
- Krupp, G., and D.C. Aumann, The origin of iodine in soil: I. Iodine in rainfall over Germany, *Chemie der Erde*, 59, 57-67, 1999.
- Laniewski, K., J. Dahlen, H. Boren, and A. Grimvall, Determination of group parameters for organically bound chlorine, bromine and iodine in precipitation, *Chemosphere*, 38 (4), 771-782, 1999.
- Lovelock, J., R.J. Maggs, and R.J. Wade, Halogenated Hydrocarbons in and over the Atlantic, *Nature*, 241 (19), 194 - 196, 1973.
- McFiggans, G., Marine aerosols and iodine emissions, *Nature*, 433 (10 February), E13, 2005.
- McFiggans, G., H. Coe, R. Burgess, J. Allan, M. Cubison, M.R. Alfarra, R. Saunders, A. Saiz-Lopez, J.M.C. Plane, D.J. Wevill, L.J. Carpenter, A.R. Rickard, and P.S. Monks, Direct evidence for coastal iodine particles from *Laminaria* macroalgae - Linkage to emissions of molecular iodine, *Atmos. Chem. Phys.*, 4, 701-713, 2004.
- McFiggans, G., J.M.C. Plane, B.J. Allan, and L.J. Carpenter, A modeling study of iodine chemistry in the marine boundary layer, *J. Geophys. Res.*, 105 (D11), 14371-14385, 2000.
- Michel, R., K. Klipsch, T.H. Ernst, M. Gorny, D. Jakob, J. Vahlbruch, H.A. Synal, and C. Schnabel, Long-lived radionuclides in the environment: On the radioecology of Iodine-129, *Radioprotection*, 40 (suppl.1), S269-S276, 2005.
- Middlebrook, A.M., D.M. Murphy, and D.S. Thomson, Observations of organic material in individual marine particles at Cape Grim during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, 103 (D13), 16475-16483, 1998.
- Moran, J.E., S. Oktay, and P.H. Santschi, Sources of iodine and iodine 129 in rivers, *Water Resour. Res.*, 38 (8), 24-1 to 24-10, 2002.
- Moran, J.E., S. Oktay, P.H. Santschi, and D.R. Schink, Atmospheric dispersal of ¹²⁹I from nuclear reprocessing facilities, *Environ. Sci. Technol.*, 33, 2536-2542, 1999.
- Murphy, D.M., D.S. Thomson, and A.M. Middlebrook, Bromine, iodine and chlorine in single aerosol particles at Cape Grim, *Geophys. Res. Lett.*, 24 (24), 3197-3200, 1997.
- Neal, C., C.J. Smith, J. Walls, P. Billingham, S. Hill, and M. Neal, Comments on the hydrochemical regulation of the halogen elements in rainfall, stemflow, throughfall, and stream waters at an acidic forested area in Mid-Wales, *Sci. Total Environ.*, 91, 1-11, 1990.
- O'Dowd, C.D., P. Aalto, K. Hämeri, M. Kulmala, and T. Hoffmann, Atmospheric particles from organic vapours, *Nature*, 416 (4 April), 497-498, 2002a.
- O'Dowd, C.D., M.C. Facchini, F. Cavalli, D. Ceburnis, M. Mircea, S. Decesari, S. Fuzzi, Y.J. Yoon, and J.P. Putaud, Biogenically driven organic contribution to marine aerosol, *Nature*, 431 (October), 676, 2004.
- O'Dowd, C.D., J.L. Jimenez, R. Bahreini, R.C. Flagan, J.H. Seinfeld, K. Hämeri, L. Pirjola, M. Kulmala, S.G. Jennings, and T. Hoffmann, Marine aerosol formation from biogenic iodine emissions, *Nature*, 417 (6 June), 632-636, 2002b.
- Orlando, J.J., Atmospheric chemistry of organic bromine and iodine compounds, in *The Handbook of Environmental Chemistry*, edited by A.H. Neilson, pp. 253-299, Springer, Heidelberg, 2003.
- Sander, R., W.C. Keene, A.A. Pszenny, R. Arimoto, G.P. Ayers, E. Baboukas, J.M. Cainey, P.J. Crutzen, R.A. Duce, G. Hönninger, B.J. Huebert, W. Maenhaut, N. Mihalopoulos, V.C. Turekain, and R. Van Dingenen, Inorganic bromine in the marine boundary layer: a critical review, *Atmos. Chem. Phys.*, 3, 1301-1336, 2003.
- Saunders, R.W., and J.M.C. Plane, Formation pathways and composition of iodine oxide ultra-fine particles, *Environ. Chem.*, 2, 299-303, 2005.
- Truesdale, V.W., and S.D. Jones, The variation of iodate and total iodine in some UK rainwater samples during 1980-1981, *J. Hydrol.*, 179, 67-86, 1996.
- Vogt, R., R. Sander, R. von Glasow, and P.J. Crutzen, Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study, *J. Atmos. Chem.*, 32, 375-395, 1999.
- von Glasow, R., and P.J. Crutzen, Tropospheric halogen chemistry, in *Treatise on Geochemistry*, edited by H.D. Holland, and K.K. Turekian, pp. 21-63, Elsevier, 2003.

White, M.L., R.K. Varner, P.M. Crill, and C.H. Mosedale, Controls on the seasonal exchange of CH_3Br in temperate peatlands, *Global Biogeochem. Cycles*, 19 (GB4009), 1-14, 2005.
 Woodcock, A.H., R.A. Duce, and J.L. Moyers, Salt particles and raindrops in Hawaii, *J. Atmos. Sci.*, 28, 1252-1257, 1971.

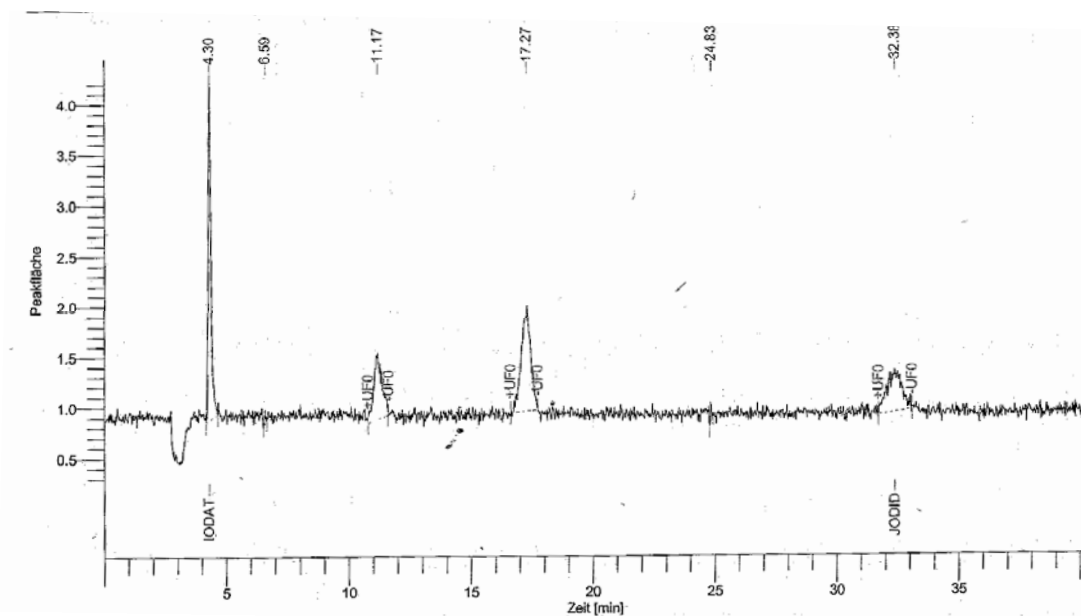
Supplementary material



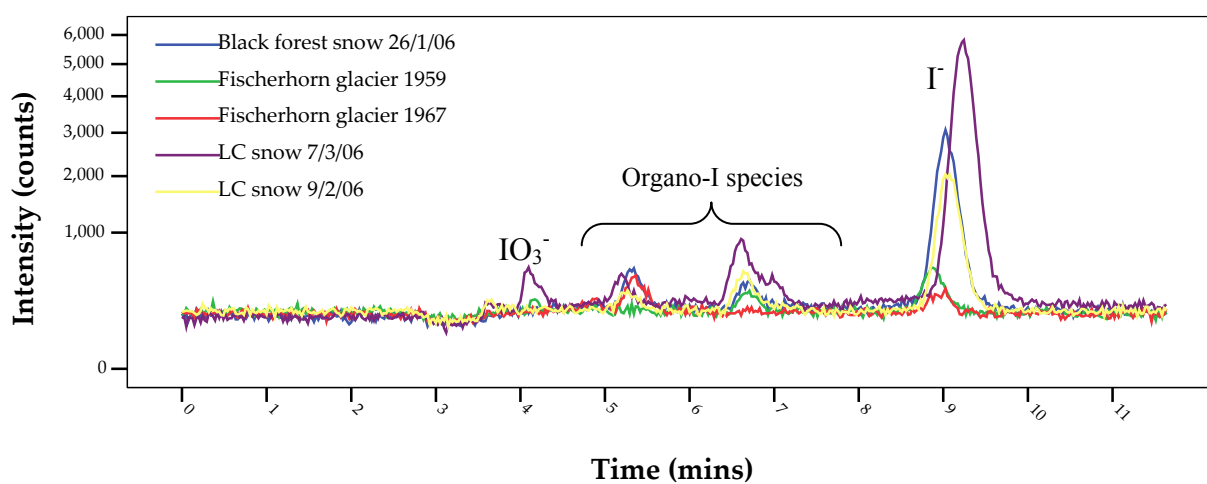
Supplementary Figure 1: Percent organically bound iodine in rainfall from Lake Constance, Germany March 2005 to February 2006. One value, collected from 5/12/05 to 29/1/06 has been excluded due to low total iodine concentrations and the long sampling period probably inflating the %-organically bound iodine.



Supplementary Figure 2: IC-ICP-MS chromatogram of a rain sample from Patagonia, Chile. This chromatogram was produced using a different software package and a column with lower resolution than the current method, hence the difference in appearance.



Supplementary material Figure 3: IC-ICP-MS chromatogram of a rain sample from Patagonia (Chile). This chromatogram was performed with an older ion exchange column, hence the longer retention time and noisier baseline. Unfortunately the electronic data for this chromatogram was lost during transition between software packages, and only the hard copy has survived. Hence the scanned version given here.



Supplementary Figure 4: IC-ICP-MS chromatograms of snow (Lake Constance, LC, and the Black Forest) and glacier ice (Fiescherhorn, Switzerland). Note the nearly identical retention time of the organo-I species in all samples shown.

Supplementary Table 1: Average total bromine, bromide, bromate, organically bound bromine, and %-organically bound bromine in rain and snow samples. All data in nmol/L except were indicated.

Sample site	Total Br	Br ⁻	BrO ₃ ⁻	Org-Br	% org-Br
Lake Constance rain (av.) n=14	44.4 (6-105)	38.7 (11-81)	7.9*	7.2 [◇] (1.8-23)	16
Lake Constance snow (av) n=15	32 (9.5-62)	29.3 (10-60)	2.4 [§]	3.8 [♣]	12
Alps rain (Sedrun) n=1	3.08	2.93	-	0.15	5
Mummelsee (snow) n=4	5.13	6.36	-	1.5	28
Patagonian peat bogs [♣] n=3	15.3	16.1	-	-	-

* only found in one rain sample after an electrical storm. [◇] excluding one negative value. [§] only found in 6 aged snow samples. [♣] excluding 5 negative values, n=10. [♣] Data from Beister et al. 2003, negative organo-Br values probably related to imprecision in our old ion exchange column.

2.2 Iodine and Bromine speciation in snow and the effect of orographically induced precipitation

B. S. Gilfedder¹, M. Petri² and H. Biester¹

1. *Institut für Umweltgeochemie, Neuenheimer Feld 236 69120 Heidelberg Germany*

2. *Bodensee-Wasserversorgung, Sipplingen Laboratory Germany*

Status: published *Atmospheric Chemistry and Physics*

Abstract

Iodine is an essential trace element for all mammals and may also influence climate through new aerosol formation. Atmospheric bromine cycling is also important due to its well-known ozone depletion capabilities. Despite precipitation being the ultimate source of iodine in the terrestrial environment, the processes effecting its distribution, speciation and transport are relatively unknown. The aim of this study was to determine the effect of orographically induced precipitation on iodine concentrations in snow and also to quantify the inorganic and organic iodine and bromine species. Snow samples were collected over an altitude profile (~840 m) from the northern Black Forest and were analysed by ion-chromatography - inductively coupled plasma mass spectrometry (IC-ICP-MS) for iodine and bromine species and trace metals (ICP-MS). All elements and species concentrations in snow showed significant ($r^2 > 0.65$) exponential decrease relationships with altitude despite the short (5 km) horizontal distance of the transect. In fact, total iodine more than halved (38 to 13 nmol/l) over the 840 m height change. The results suggest that orographic lifting and subsequent precipitation has a major influence on iodine concentrations in snow. This orographically induced removal effect may be more important than lateral distance from the ocean in determining iodine concentrations in terrestrial precipitation. The microphysical removal process was common to all elements indicating that the iodine and bromine are internally mixed within the snow crystals. We also show that organically bound iodine is the dominant iodine species in snow (61-75 %), followed by iodide. Iodate was only found in two samples despite a detection limit of 0.3 nmol/l. Two unknown but most likely anionic organo-I species were also identified in IC-ICP-MS chromatograms and comprised 2-10 % of the total iodine. The majority of the bromine was inorganic bromide with a max. of 32 % organo-Br.

2.2.1 Introduction

Iodine is an essential nutritional element for all mammals, including humans. A lack of dietary iodine intake can lead to iodine deficiency disorders such as goiter and in more severe cases, cretinism, which can cause both mental and physical disabilities (Dobson, 1998; WHO, 2004; Slavin, 2005). Iodine transport from the oceans by clouds and aerosols and subsequent precipitation as rain or snow is one of the primary factors influencing iodine levels and availability on the continents (Whitehead, 1984; Fuge and Johnson, 1986; Krupp and Aumann, 1999; Moran et al., 2002). However, there is also conflicting evidence regarding the terrestrial processes effecting

iodine concentrations in rainfall and particularly with the suggestion that iodine levels decrease with distance from the ocean (Fuge and Johnson, 1986; Krupp and Aumann, 1999; Schnell and Aumann, 1999; Slavin, 2005). Most studies concentrate on lateral distances and to the best of our knowledge there has been only one other study focusing on the influence of orographically induced precipitation on iodine levels in rainfall (Duce et al., 1965). Iodine in rainfall is not a simple product of sea spray as observed for Cl, with large (100-10 000) enrichment factors in both rain and aerosols compared to ocean water (Duce et al., 1965; Duce et al., 1967; Winchester and Duce, 1967; Woodcock et al., 1971; Sturges and Barrie, 1988). Bubble bursting and ejection of iodine rich material from the ocean surface microlayer is one possible mechanism for the iodine enrichments (Seto and Duce, 1972), although this can only produce, at maximum, an enrichment factor of ~50. Therefore, condensation of gaseous biogenic iodine compounds onto (or forming) aerosols is required to explain the large iodine enrichments observed in aerosols and rainfall (Woodcock et al., 1971; Moyers and Duce, 1972; Duce and Hoffman, 1976; O'Dowd et al., 2002; Baker, 2005). Although research on iodine in rainfall is still limited, iodine levels and particularly speciation in snow is almost non-existent. Snow is an important factor in the hydrological cycle during winter at higher latitudes and as such warrants further attention. One explanation for the lack of speciation data is undoubtedly the very low concentrations of individual iodine species in rain and snow and therefore methods for reliable speciation are often complex or unavailable. However, with the wide spread use of ICP-MS and the ability to couple an ion chromatograph to this extraordinarily sensitive instrument (Heumann et al., 1998; Gilfedder et al., 2007) it is possible to measure anionic iodine and bromine species down to sub nmol concentrations. One of the features of this method is that many interfering ions, such as Cl, are separated from the element of interest and therefore the sensitivity of individual species is even greater than observed for total concentrations. Iodine speciation is also of interest for atmospheric iodine cycling as there is a discrepancy between most model calculations, which suggest that iodate should be the dominant iodine species in the particulate phase (Vogt et al., 1999; McFiggans et al., 2000), and field observations which show that organically bound iodine and iodide are the dominant iodine species (Baker et al., 2001; Baker, 2004, 2005; Gilfedder et al., 2007). Recent modeling work to reconcile this discrepancy further highlights the potential importance of organo-I in atmospheric chemistry cycles (Pechtl et al., 2007). For example, organo-I has implications for the sea/atmosphere fractionation mechanism that concentrates iodine in aerosols and rain and perhaps for iodine's effectiveness in destroying tropospheric ozone (Duce and Hoffman, 1976; Calvert and Lindberg, 2004; Baker, 2005). Bromine is also of interest in atmospheric research due to (1) its well-known ozone depletion capabilities, and (2) the interesting observation that activated bromine (Br_2) is liberated from larger size aerosols causing bromine depletion relative to seawater, whereas small aerosols tend to be enriched in bromine (Sander et al., 2003). In this work we investigate the

changes in iodine and bromine species (including the organically bound fraction), and metal concentrations in snow with altitude. The primary aims of this study are to clarify the role of microphysical landscape features (mountains) and the associated atmospheric processes (orographically induced precipitation) on the distribution of iodine and bromine as well as determine the dominant iodine species in snow.

2.2.2 Methods

A transect for snow sampling was selected in the northern Black Forest between the village of Ottenhöfen (326 masl) and the summit of the highest peak in the area; 'Hornisgrinde' (1164 masl). This transect was chosen to minimize the horizontal distance (5 km) and maximize changes in elevation. Fresh snow was collected on the 11th and 12th of February 2006 in new LDPE bottles at selected locations between Ottenhöfen and Hornisgrinde along the hiking track 'Elsa Weg'. Back trajectories (HYSPLIT model; <http://www.arl.noaa.gov/ready/hysplit4.html>) of air masses arriving at the site were calculated for the previous six days with a new trajectory starting each day at 0h UTC using an altitude of 500m above ground level and the FNL meteorological database (Fig. 1). The data show that the majority of the precipitation sampled was derived from the Atlantic Ocean. Also, the weather system had passed from the low lands to the west of the sampling site before being orographically lifted over the Black Forest mountain range. All samples were collected from open areas and clearings in the forest. Four samples were also taken on 26 January 2006 at a height of 1034 masl (Mummelsee) and again four additional samples were taken in mid April (14/04/06) from very old snow deposits at 796 masl and above on the same transect. This remnant snow was only present due to the elevation and all snow from lower altitudes had previously melted. It appeared to be recrystallised into small ice particles and had probably undergone partial melting and refreezing. It also contained small debris from the surrounding forest on the surface which was discarded by filtering. The snow was thawed, filtered (0.45 µm) and stored at 4°C until analysed (max. 1 month). It has been shown that no significant changes in iodine speciation occur in samples stored for up to two months (Campos, 1997). Samples were allowed to warm to room temperature and were then analysed for total iodine and bromine by an inductively coupled plasma–mass spectrometer (ICP-MS). For iodine we scanned on the only stable isotope, ¹²⁷I, and for bromine on the ⁷⁹Br isotope. ¹⁸⁷Re was added to the samples as an internal standard. Iodine and bromine species (iodide, iodate, bromide, bromate and organically bound I/Br) were analysed by coupling an ion chromatograph to the ICP-MS (IC-ICP-MS). Organically bound iodine and bromine was calculated as total iodine minus the sum of the inorganic species (i.e. Org-I = total I – (I⁻ + IO₃⁻)).

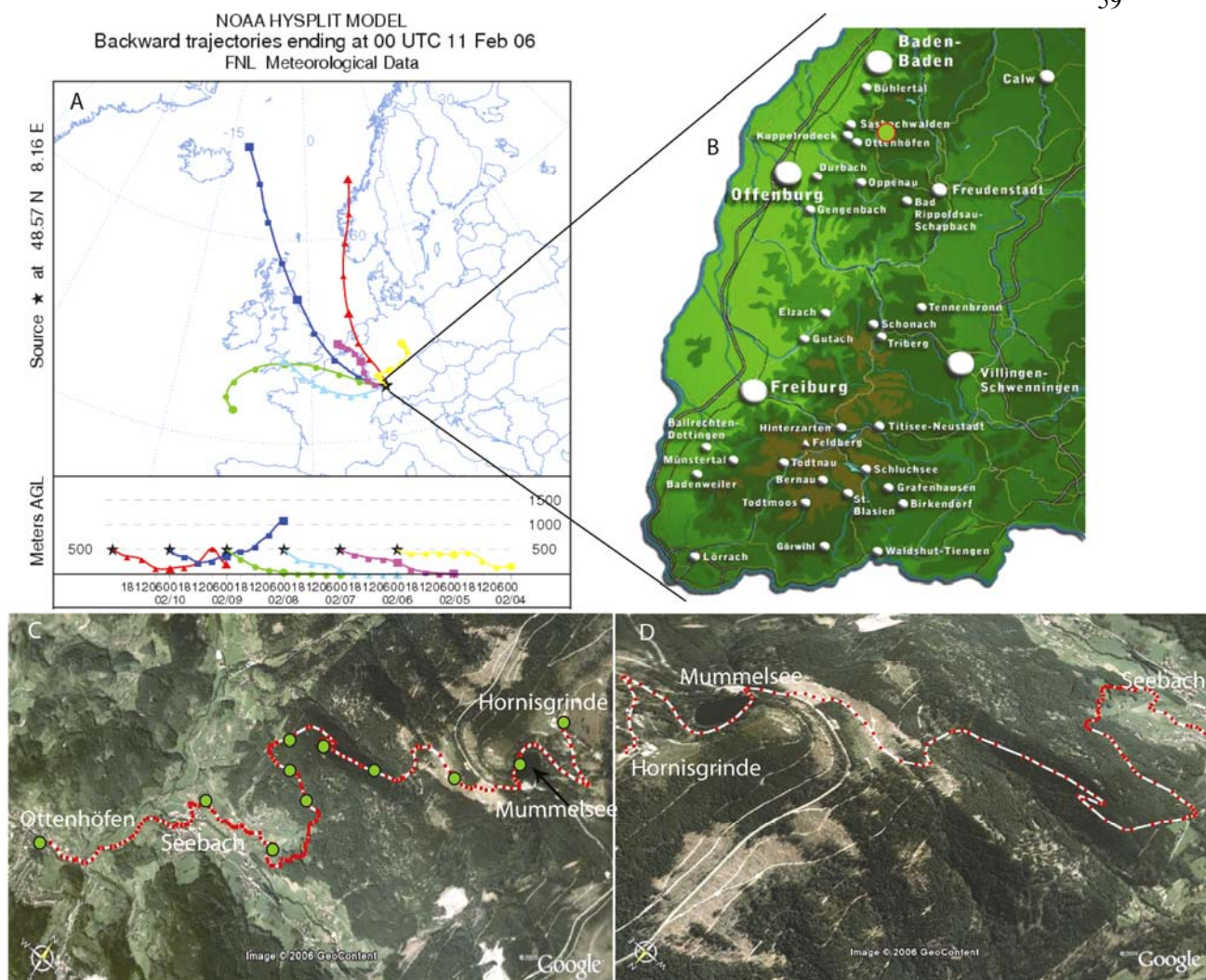


Fig. 1: A) Europe map with sampling site and 6 day back trajectory for air parcels arriving at Ottenhöfen, B) The Black Forest mountain range and sampling site, C and D) Sampling transect and sampling sites (green circles) from Ottenhöfen (326 masl) to Hornisgrinde (1164 masl).

Iodine and bromine species were quantified using a Dionex AS16 column with an AG16 guard column, 35 mmol NaOH eluent, a flow rate of 0.9 ml/min and a Meinhard nebulizer with a cyclone spray chamber on a Perkin Elmer quadrupole ICP-MS. Samples were injected into the chromatographic system with a Perkin Elmer series 200 autosampler. This method has a detection limit for aqueous iodine species of about 0.3 nmol/l and each sample has a run-time of only 12 minutes. Moreover, no sample pretreatment is required. Unidentified organic iodine species were observed in all chromatograms; while not strictly correct these species have been quantified based on the iodide calibration curve. This should not pose a large problem as all iodine atoms are converted to I^+ in the plasma prior to quantification with the mass spectrometer. Precision was checked for total iodine and bromine by running replicates of samples from 326, 400, 560, 597, 614 masl and triplicate analysis of the sample from 478 masl. The maximum relative standard deviation (RSD) for iodine was 1.3 % which equated to a concentration standard deviation (SD) of ± 0.45 nmol/l. For bromine the highest RSD was 4.8 % with an associated SD of ± 4.9 nmol/l. As

such, a RSD of 1.3 % for iodine and 4.7 % for bromine was used for propagation of errors for samples where no replicates were analysed. No replicates were made for speciation, however this method (based on our experience and from other IC-ICP-MS studies (Heumann et al., 1994)) consistently has a RSD less than 2 % for iodine species and between 5-7 % for bromide. As such we have adopted a RSD value of 2 % for iodine species and 7 % for bromide when propagating errors for calculation of organo-I and organo-Br. The accuracy of total iodine, total bromine, bromide, and iodide concentrations were checked using standard reference material BCR-611. BCR-611 is a groundwater reference material with a certified bromide level of $93 \pm 4 \mu\text{g/l}$. It also gives indicative values for total bromine ($107 \pm 11 \mu\text{g/l}$), total iodine ($9.3 \pm 1.3 \mu\text{g/l}$), and iodide ($9.0 \pm 1.1 \mu\text{g/l}$). More information on this reference material can be found at the European Institute for Reference Materials and Measurements website: <http://www.irmm.jrc.be>. All of our values were consistently within the error given in the certificate except for total bromine which was slightly lower (bromide $93.5 \mu\text{g/l}$, total bromine $94 \mu\text{g/l}$, iodide $9.4 \mu\text{g/l}$, and total iodine $9.65 \mu\text{g/l}$). We believe that our value for total bromine is more realistic than the reference material average of $107 \mu\text{g/l}$, as this high concentration would imply a relatively large proportion of organically bound bromine in the groundwater, which is unlikely. After withdrawal and analysis of the halogens the remaining snowmelt was acidified to $\text{pH} < 2$ with suprapur[®] nitric acid and stored at 4°C . The samples were analysed for total metals (Li, V, Mn, Co, Rb, Zn, As, Mo, Pb, Ba, Sb, and U) 3 months after acidification with the ICP-MS. RSDs for metals using this method was lower than 8 %, usually around 2 %. Standard reference material TM-23.2 from Environment Canada's national water research institute was used to check the accuracy of the metal analysis after dilution by a factor of 10 to ensure that the concentrations were similar to that in the snow. This lake water reference material is certified for Pb, Sb, Mo, As, Ba, Co, Mn, U, and V. All analysed values were well within the error given in the certificate and deviated from the average certificate value by less than 10 %. More information on this reference material can be found on the Environment Canada webpage: <http://www.nwri.ca/nlet/crm-e.html>. Sodium was analysed by a Perkin Elmer flame AAS after the acidification. Standard deviations were calculated from five consecutive injections.

2.2.3 Results

Total iodine concentrations in snow samples were slightly higher than or similar to other existing studies (Duce et al., 1965; Jickells et al., 1991; Moran et al., 1999; Gilfedder et al., 2007), but decreased exponentially with increasing elevation ($r^2 = 0.85$; Fig. 2a). Over the 838 m height change from Ottenhöfen (326 masl) to Hornisgrinde (1164 masl) total iodine levels decreased from a maximum of 38 nmol/l to 13 nmol/l , respectively.

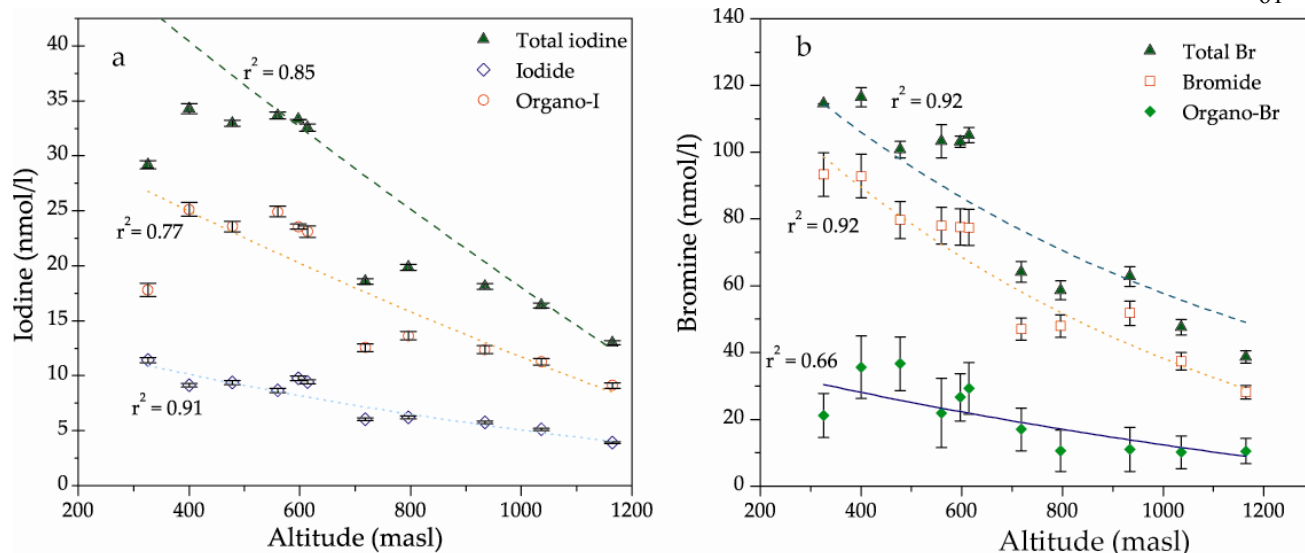


Fig. 2: a) Total iodine, iodide, and organically bound iodine in snow vs. altitude. b) Total bromine, bromide, and organically bound Br in snow vs. altitude. All data points are from the 11th and 12th of February 2006 and fitted with exponential decay functions. Error bars represent analytical precision and were calculated as 1σ of replicate analysis.

IC-ICP-MS iodine speciation analysis showed similar results to total iodine. Iodide concentrations decreased exponentially with increasing altitude from 11.4 nmol/l at Ottenhöfen to 3.9 nmol/l at Hornisgrinde ($r^2=0.92$; Fig. 2a). No iodate was observed in any of these snow samples. Organically bound iodine also decreased with altitude, with maximum concentrations at Seebach (400 masl; 28.8 nmol/l) and then steadily decreased to 9.1 nmol/l at Hornisgrinde (Fig. 2a). Organically bound iodine was the most abundant iodine species in all samples (61-75 % of total iodine), with no clear change in percentages with altitude (Supplementary Fig. 1). Interestingly, two unidentified organo-I species were consistently found in IC-ICP-MS chromatograms in all snow samples between the iodide and iodate peaks (Fig. 3). It is thought that these peaks are anionic organic iodine compounds due to their consistent separation by the anion exchange column and stable behavior. The larger of the two peaks had a retention time of 6.8 minutes and the smaller peak eluted at a slightly shorter time of 5.4 minutes. These peaks generally accounted for 5-10 % of the total iodine concentrations and also displayed an inverse relationship with altitude (Supplementary material Table 1).

Total bromine concentrations showed much the same pattern as iodine, decreasing exponentially with altitude from 129 nmol/l at Seebach to 38.8 nmol/l at Hornisgrinde (Fig. 2b). Bromide was also inversely correlated with altitude with an r^2 value of 0.92. Organically bound bromine was not so well correlated with altitude ($r^2=0.66$), however the trend is still clear, as with all other species: exponentially decreasing concentrations with increasing altitude. Percent organically bound bromine displayed no relationship with altitude ($r^2=0.02$; data not shown). In contrast to iodine, the majority of bromine in snow was inorganic bromide (68-81 %). Bromate was not observed in any of the samples, whereas organically bound bromine accounted for 18-32% of the total bromine.

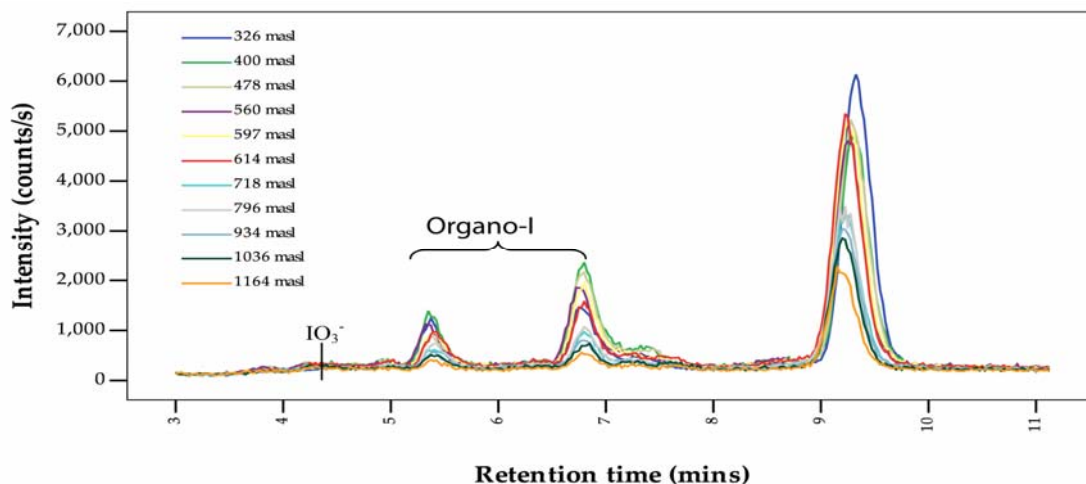


Fig. 3: IC-ICP-MS chromatogram of iodine species in snow. Iodate less than 0.3 nmol/l. Largest iodide peak 11.4 nmol/l.

Metal concentrations also decreased exponentially with altitude (Fig. 4 and supplementary material Fig. 2). In fact, many of the metals even showed a stronger inverse relationship with altitude than iodine and bromine. Also, significant positive ($p < 0.001$) correlations between all elements, including iodine and bromine, were observed (Table 1 and Supplementary material Table 1).

Table 1: Selected correlation coefficients (r) between iodine, bromine, and metals.

Elements	r	Element	r
I-Br	0.97	Br-Na	0.86
I-Li	0.92	Br-Li	0.96
I-V	0.98	Br-V	0.98
I-Mn	0.88	Br-Mn	0.95
I-Co	0.82	Br-Rb	0.90
I-Pb	0.897	Br-As	0.95
I-Ba	0.90	Br-Pb	0.96
I-Sb	0.90	Br-Ba	0.93
I-U	0.92	Br-Sb	0.96

Total iodine concentrations in the four snow samples taken in January from the surface of a small frozen lake at 1036 masl (Mummelsee) were similar (although slightly lower) to those taken in February. Organo-I accounted for 53-62 % of the total iodine in these samples and again no iodate was observed. The only notable observation for bromine from these samples is that the percent organically bound bromine is nearly identical to all other samples and is therefore relatively invariant with time (ca. 30%). The snow sampled in April contained significantly lower iodine (av. 3.9 nmol/l) and bromine (av. 33.4 nmol/l) concentrations than the previous sampling tours and showed no significant relationship with altitude. These anomalously low results are undoubtedly due to partial melting and refreezing and other post depositional changes. It is thought that, due its

large ionic radii, iodine is excluded from the recrystallizing ice and hence is preferentially leached from the snow during partial melting. Organo-I composed approximately 50 % of the total iodine with iodide being the next most abundant species. Iodate was also observed in two chromatograms, although it was only responsible for at maximum 16 % of the total iodine. Interestingly, we also observed the same unidentified iodine peak (retention time 6.8 minutes) between the iodate and iodide peaks as noted above. This suggests that this species is stable and can remain in the snow during melting-refreezing events.

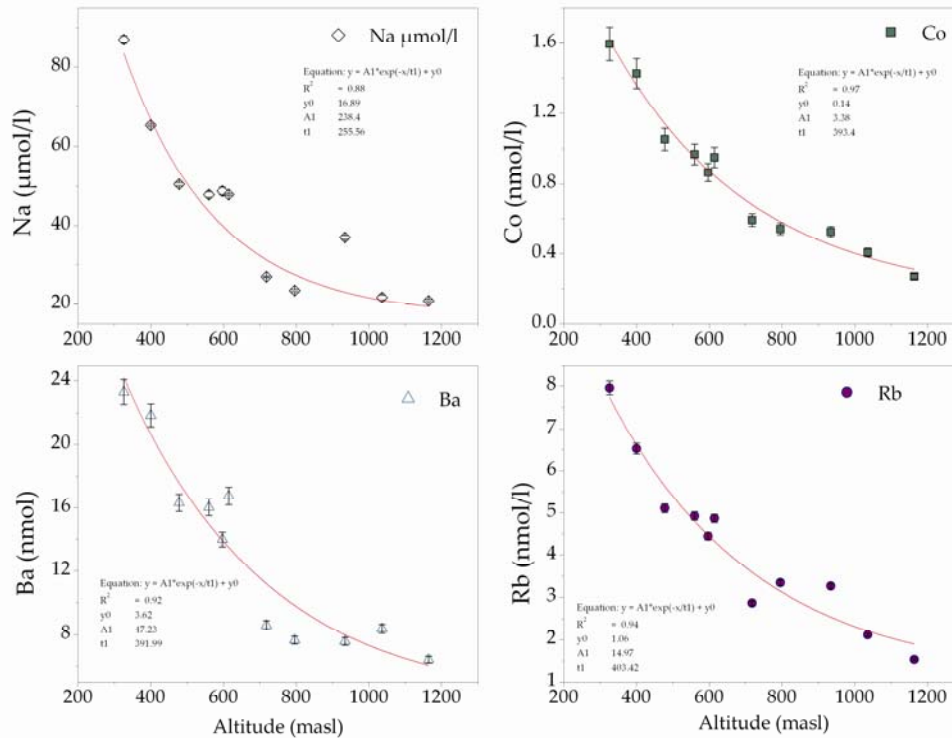


Fig. 4: Sodium, Co, Ba and Rb concentrations in snow vs. altitude in the northern Black Forest, Germany. Fitted with exponential decay functions. Error bars represent analytical precision and were calculated as 1σ of replicate analysis.

Molar iodine and bromine enrichment factors (EF) relative to seawater may be able to trace the origin of these elements (Winchester and Duce, 1967; Woodcock et al., 1971; Gilfedder et al., 2007). EFs are calculated by dividing the halogen to sodium ratios in snow by halogen to sodium ratios in seawater (e.g. I/Na in snow divided by I/Na seawater). When these enrichment factors are calculated, it is immediately apparent that iodine is highly enriched in snow (average EF 204, max 281). EFs appear to increase linearly with elevation until 796 masl ($r^2=0.95$), whereafter the relationship is less clear (Fig. 5). If the sample from 934 masl is excluded and a 2nd order polynomial is fitted to the data it appears that the iodine EFs decrease after ~ 800 masl ($r^2 = 0.87$). However, this is only based on the last two sample points and further studies are needed to confirm or refute this decrease in EF at higher altitudes. In contrast to iodine, bromine enrichment factors range from slightly depleted (0.7) at Ottenhöfen to no enrichment or only slightly enriched over

the remainder of the transect (max. 1.4). Bromine enrichment factors also increases linearly with altitude ($r^2=0.84$) up to 796 masl, whereafter the relationship again appears to decrease if the point from 934 masl is removed ($r^2=0.8$; Fig. 5). In part the anomalous trend in these last three points is due to Na following a decrease curve with a significantly different ‘decay’ constant than iodine and bromine. We can also calculate iodine enrichment factors relative to bromine (I/Br in snow divided by I/Br in seawater). These EFs (av. 602, max 665) show that iodine is more enriched relative to bromine than to sodium, however there is no relationship with altitude ($r^2=0.3$; data not shown). Enrichment factors for iodine relative to bromine from the January samples were lower than those taken in February, averaging 402.

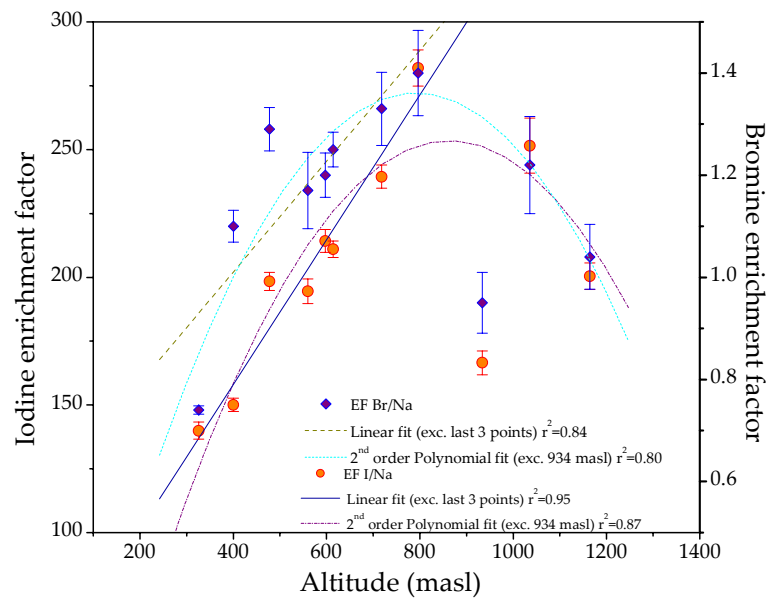


Fig. 5: Iodine enrichment factors relative to seawater Na concentrations. Linear fit is excluding the last 3 samples whereas the polynomial is excluding the sample from 934 masl

2.2.4 Discussion

2.2.4.1 Microphysical processes

There is growing evidence that suggests iodine concentrations in rainfall are not simply related to distance from the ocean (Krupp and Aumann, 1999; Moran et al., 1999; Michel et al., 2002). While back trajectories are not given in any of these studies and the authors assume that the closest ocean is the source of rainfall, the data still appears to be relatively robust. The data presented here indicates that, compared to lateral distance, removal by orographically induced precipitation has a large effect on the total iodine concentrations as well as the individual iodine species in snow. In fact, iodine concentrations more than halve over a horizontal distance of only 5 km and a vertical change of ~ 800 m. Duce et al., (1965) found a relatively linear inverse relationship between height (and thus a decrease in vapor pressures and assumingly an increase in the precipitation rate) and iodine concentrations in Hawaii, however the scatter in their data points was much greater than observed in this study. Interestingly, Reithmeier et al., (2006) have also

suggested recently that, based on differences in ^{129}I concentrations between Zürich and the Fiescherhorn (~4000 masl) glacier Switzerland, radiogenic iodine is removed with increasing altitude. Moreover, the systematic exponential decrease in concentration is not confined solely to iodine and bromine as the 12 metals also analysed displayed a similar pattern. Our data suggest that depletion of elements due to orographic lifting and removal by precipitation is a general atmospheric microphysical processes rather than element specific. This is supported by the significant correlations between all of the elements, which also indicate that iodine, bromine and metals are internally mixed within the snow crystals. Such an altitude dependence for iodine is perhaps not unexpected considering that some of the areas most effected by iodine deficiency disorders are (or in some cases, were, before introduction of iodinated salt) located in mountainous regions such as the Alps or the Himalayas (Stewart, 1990; Slavin, 2005). Perhaps the altitude that a weather system must pass over, and thus the degree of orographically induced precipitation exerted on this system, will have the largest influence on iodine concentrations in rainfall rather than the lateral distance traveled.

All elements appear to follow an exponential decrease curve. It is especially difficult to model this complex system without significantly more data such as updraft velocity, droplet size distributions, riming potential, temperature at the time of precipitation, atmospheric pressure, and aerosol chemistry and distributions etc. It is even possible that two effects are occurring in unison to lower the iodine, bromine and metal levels with increasing altitude; the rainout and depletion effect suggested above, and also dilution due to condensation of water vapor (obviously iodine free) onto the snow crystals as the cloud parcel rises and cools. The rainout effect continually removes a portion of the 'total' iodine available to precipitate, whereas the rate of the second, dilution effect, would increase with altitude due to the decreasing vapor pressure associated with lifting and cooling of the cloud mass. If we conceptually parameterize rainout the processes with arbitrary values (i.e. a set amount of iodine in the cloud is available to precipitate and the removal rate is constant with altitude) then iodine levels in the snow should decrease following an exponential decrease relationship similar to that observed here. This model is, however, undoubtedly too simplistic and should be further refined when more results are available. The second 'dilution' possibility is more complicated to model, as modeling droplet (or snowflake) growth requires considerably more variables than measured here and is unfortunately out of the scope of this work. However, we suggest that future projects monitor such variables as vapor pressure, updraft speed, and supersaturation so that the possibility of a dilution effect due to growth from the vapor phase can be assessed.

2.2.4.2 Speciation

Iodine is of particular interest in atmospheric chemistry due to its possible role in new aerosol formation (O'Dowd et al., 2002), tropospheric ozone depletion (von Glasow and Crutzen, 2003; Calvert and Lindberg, 2004), atmosphere-ocean interactions (Duce and Hoffman, 1976) and more generally as an important constituent of tropospheric chemical cycles. While there has been a large research effort to quantify the gaseous iodine flux species from the ocean and their role in new particle formation in recent years, most of these studies have concentrated on inorganic speciation in the particulate and aqueous phase. Indeed, the majority of atmospheric models indicate that iodate should be the only stable long-term iodine species in particles and the aqueous phase, although more recent attempts have begun to tackle this problem by incorporating an organic fraction (Vogt et al., 1999; McFiggans et al., 2000; Saiz-Lopez et al., 2006; Pechtl et al., 2007). However, it is becoming apparent that organically bound iodine is a major, if not the most important iodine species in small aerosol particles, rain, and snow (Baker et al., 2000; Baker, 2005; Gilfedder et al., 2007). It is obvious from the data presented here that organically bound iodine is the dominant species in snow from the northern Black Forest, accounting for between 60-75% of total iodine. To date, there appears to be three plausible mechanisms for the formation of organically bound iodine in the atmosphere; 1) ejection of iodo-organic rich material from the ocean surface micro-layer into the atmosphere during bubble bursting, whereafter the small droplets evaporate leaving a small aerosol which may subsequently deliquesce and become a cloud droplet (Seto and Duce, 1972; Cavalli et al., 2004); 2) biogenic iodine gases emitted from the ocean (e.g. CH_3I , I_2 or CH_2I_2) are photolysed to I° which, after a series of reactions, ends up as IO , I_2 or HOI (von Glasow and Crutzen, 2003). These species may easily bind to atmospheric organic material, either gaseous (e.g. terpenes and/or isoprene (Greenberg et al., 2005)) or particulate matter; 3) Biogenic terrestrial organo-I emissions (Dimmer et al., 2000); these can probably be neglected in this study due to very little terrestrial biological productivity during the European winter. The second mechanism may reduce the impact of iodine on ozone depletion in the troposphere by reactions between highly reactive iodine species and organic material. Mechanisms 1 and 2 could also be occurring simultaneously, which may lead to two organically bound fractions, those associated with secondary iodo-organics, and those associated with higher molecular weight material from the ocean surface. An interesting finding is the two unknown, most likely organic, peaks observed in the snow IC-ICP-MS chromatograms. These same species have also been observed in rain from Lake Constance, Germany, Patagonia, Chile and in a glacier core from the Fiescherhorn glacier (Gilfedder et al., 2007). This supports our earlier suggestion that these are important iodine species in the atmosphere, and may even be globally ubiquitous. Unfortunately, it has not been possible to identify these peaks with the standards available to date.

These species may be formed by photolysis of iodo-organics derived from primary aerosols or by secondary gas phase-particle phase reactions.

The majority of the total bromine is bromide, of which the majority is most likely from ocean water as suggested by relatively little depletion or enrichment compared to this source. The organically bound bromine in snow (max. 32%) may be derived from the ocean surface layer as discussed above for iodine or between reactive bromine species such as BrCl and organic material.

2.2.4.3 Origin of the iodine and bromine

Finally we consider the enrichment factors and the possible origin of iodine in snow. Iodine in snow is highly enriched relative to both iodine/bromine and iodine/sodium ratios in seawater. Similar enrichments are well documented in marine aerosols and rain samples and is thought to be a function of both fractionation at the ocean surface during bubble breaking and emissions of biogenic iodine gases (Duce et al., 1965; Duce et al., 1967; Woodcock et al., 1971; Sturges and Barrie, 1988; Baker, 2004, 2005). The observation that the snow sampled here display almost identical enrichment factors as marine aerosols (Duce et al., 1965; Baker, 2005) tend to suggest that iodine and bromine in snow originate from deliquescence and growth of these aerosols. As such, we hypothesize that iodine is transported to the continents from the ocean primarily by aerosols and aerosol derived droplets. It is interesting to note that iodine enrichment factors in precipitation are also large in the winter, when biological productivity in the ocean is generally low at mid to high latitudes (O'Dowd et al., 2004). This suggests that at least a part of the enrichment is due to physical mechanisms such as bubble bursting rather than purely biological. As mentioned above, it is likely that the enrichment of iodine in aerosol, rain, and snow is related to both biological and physical mechanisms.

2.2.5 Conclusion

Iodine is an essential element for all mammals and may also be involved in new aerosol formation. We have presented here iodine and bromine speciation and total metal concentrations in snow over an altitude profile ranging from 326 to 1164 masl in the northern Black Forest. Iodine species (total I, I⁻ and organo-I), bromine species (total Br, Br⁻, and organo-Br) and metals decreased exponentially over the height change within only 5 km horizontal distance. In fact iodine concentrations more than halve over this distance. Therefore, it is suggested that orographic lifting of cloud masses and subsequent removal by precipitation is the major influencing factor on iodine and bromine concentrations in precipitation. This may reconcile previous data, which has been ambiguous as to the relationship between iodine concentrations in rainfall and distance from the coast. It is proposed that orographic cloud lifting and the intense precipitation this often produces

by rapid cooling of the air mass may be the dominant influence on terrestrial iodine rather than horizontal distance.

Iodine:sodium ratios in snow from the northern Black Forest indicate that iodine is highly enriched compared to iodine:sodium ratios in ocean water, whereas bromine ranges from slightly depleted to slightly enriched relative to seawater. Based on these enrichment factors and their resemblance to marine aerosol it is proposed that iodine and bromine in snow are derived from deliquescence of marine aerosol and subsequent growth into snow crystals.

In contrast to most atmospheric models, which predict iodate as the only stable iodine species in particulate and aqueous phases, organically bound iodine was the most abundant iodine species in snow, followed by iodide. No iodate was found in the snow samples from January or February although a small amount was observed in two samples of very old snow in April. The organic iodine probably originates from a combination of 1) ejection of iodine-rich material from the oceanic microlayer into the atmosphere as well as 2) addition of gaseous or (gas phased derived) reactive iodine species to preexisting organic molecules. Active species such as HOI, I₂ and IO are likely candidates for such reactions. It is clear from this and previous studies that organic iodine is an important part of the atmospheric iodine cycle and as such warrants further attention.

Acknowledgments

This project was funded by the Deutsche Forschungsgemeinschaft BI 734/5-1/2 to Harald Biester. B.S.G would also like to thank my colleagues and two anonymous reviewers who significantly improved earlier versions of this manuscript.

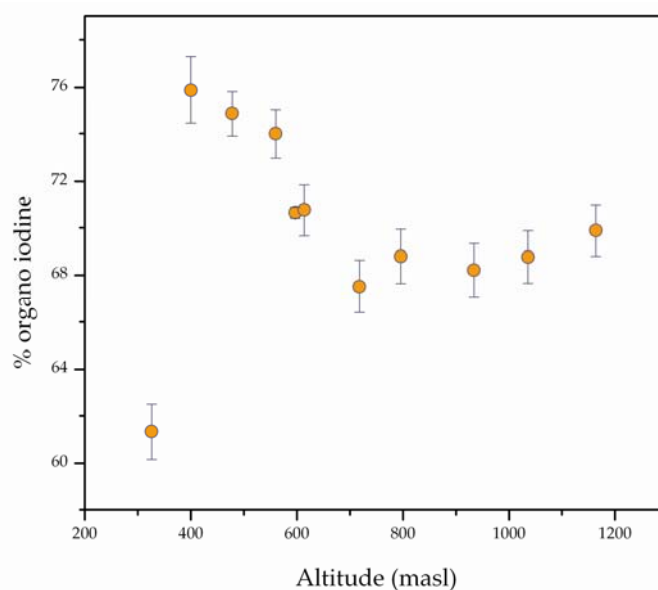
2.2.6 References

- Baker, A.R.: Inorganic iodine speciation in tropical Atlantic aerosol, *Geophys. Res. Lett.*, 31, doi: 10.1029/2004GL020144, 2004.
- Baker, A.R.: Marine aerosol iodine chemistry: the importance of soluble organic iodine, *Environ. Chem.*, 2, 295-298, 2005.
- Baker, A.R., Thompson, D., Campos, A.M., Parry, S.J. and Jickells, T.D.: Iodine concentrations and availability in atmospheric aerosol, *Atmos. Environ.*, 34, 4331-4336, 2000.
- Baker, A.R., Tunnicliffe, C. and Jickells, T.D.: Iodine speciation and deposition fluxes from the marine atmosphere, *J. Geophys. Res.*, 106, 28743-28749, 2001.
- Calvert, J.G. and Lindberg, S.E.: Potential influence of iodine-containing compounds on the chemistry of the troposphere in the polar spring. I. Ozone depletion, *Atmos. Environ.*, 38, 5087-5104, 2004.
- Campos, M.L.A.M.: New approach to evaluating dissolved iodine speciation in natural waters using cathodic stripping voltammetry and a storage study for preserving iodine species, *Mar. Chem.*, 57, 107-117, 1997.
- Cavalli, F., Facchini, M.C., Decesari, S., Mircea, M., Emblic, L., Fuzzi, S., Ceburnis, D., Yoon, Y.J., O'Dowd, C.D., Putaud, J.P. and Dell'Acqua, A.: Advances in characterization of size-

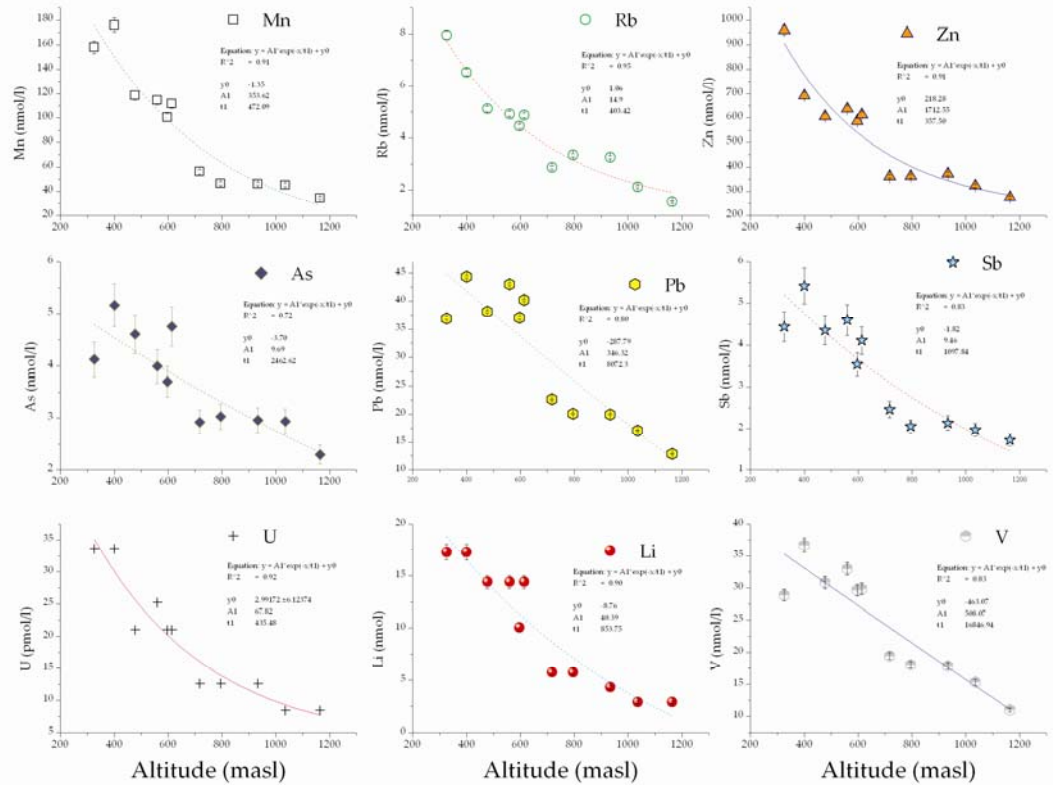
- resolved organic matter in marine aerosol over the north Atlantic, *J. Geophys. Res.*, 109, 1-14, 2004.
- Dimmer, C.H., Simmonds, P.G., Nickless, G. and Nickless, M.R.: Biogenic fluxes of halomethanes from Irish peatland ecosystems, *Atmos. Environ.*, 35, 321-330, 2000.
- Dobson, J.E.: The iodine factor in health and evolution, *The Geographical Review*, 88, 1-28, 1998.
- Duce, R.A. and Hoffman, E.J.: Chemical fractionation at the air/sea interface, *Annu. Rev. Earth Planet. Sci.*, 4, 187-228, 1976.
- Duce, R.A., Winchester, J.W. and Van Nahl, T.W.: Iodine, bromine, and chlorine in the Hawaiian marine atmosphere, *J. Geophys. Res.*, 70, 1775-1799, 1965.
- Duce, R.A., Woodcock, A.H. and Moyers, J.L.: Variation of ion ratios with size among particles in tropical oceanic air, *Tellus*, XIX, 369-379, 1967.
- Fuge, R. and Johnson, C.C.: The geochemistry of iodine - a review, *Environ. Geochem. Health*, 8, 31-54, 1986.
- Gilfedder, B.S., Petri, M. and Biester, H.: Iodine speciation in rain and snow: Implications for the atmospheric iodine sink, *J. Geophys. Res.*, 112, doi:10.1029/2006JD007356, 2007.
- Greenberg, J.P., Guenther, A.B. and Turnipseed, A.: Marine organic halide and isoprene emissions near Mace Head, Ireland, *Environ. Chem.*, 2, 219-294, 2005.
- Heumann, K.G., Gallus, S.M., Rädlinger, G. and Vogl, J.: Accurate determination of element species by on-line coupling of chromatographic systems with ICP-MS using isotope dilution technique, *Spectrochim. Acta part B*, 53, 273-287, 1998.
- Heumann, K.G., Rottmann, L. and Vogl, J.: Elemental speciation with liquid chromatography-inductively coupled plasma isotope dilution mass spectrometry, *J. Anal. At. Spectrom.*, 9, 1351 - 1355, 1994.
- Jickells, T.D., Davies, T.D., Tranter, M., Landsberger, S., Jarvis, K. and Abrahams, P.: Trace elements in snow samples from the Scottish Highlands: Sources and dissolved/particulate distributions, *Atmos. Environ.*, 26A, 393-401, 1991.
- Krupp, G. and Aumann, D.C.: The origin of iodine in soil: I. Iodine in rainfall over Germany, *Chem. Erde*, 59, 57-67, 1999.
- McFiggans, G., Plane, J.M.C., Allan, B.J. and Carpenter, L.J.: A modeling study of iodine chemistry in the marine boundary layer, *J. Geophys. Res.*, 105, 14371-14385, 2000.
- Michel, R., Ernst, T.H., Jakob, D., Klipsch, K., Szidat, S., Synal, H.A. and Schnabel, C.: Long-lived radionuclides in the environment: The case of iodine-129. *EUROSAFE*, http://www.eurosafe-forum.org/products/data/5/pe_235_24_1_euro2_4_2_iodine129.pdf?PHPSESSID=933dfc3de630a555e394b81657d2af29, Berlin (2002).
- Moran, J.E., Oktay, S. and Santschi, P.H.: Sources of iodine and iodine 129 in rivers, *Water Resour. Res.*, 38, 24-21 to 24-10, 2002.
- Moran, J.E., Oktay, S., Santschi, P.H. and Schink, D.R.: Atmospheric dispersal of ¹²⁹I from nuclear reprocessing facilities, *Environ. Sci. Technol.*, 33, 2536-2542, 1999.
- Moyers, J.L. and Duce, R.A.: Gaseous and particulate iodine in the marine atmosphere, *J. Geophys. Res.*, 77, 5229-5238, 1972.
- O'Dowd, C.D., Facchini, M.C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y.J. and Putaud, J.P.: Biogenically driven organic contribution to marine aerosol, *Nature*, 431, 676, 2004.
- O'Dowd, C.D., Jimenez, J.L., Bahreini, R., Flagan, R.C., Seinfeld, J.H., Hameri, K., Pirjola, L., Kulmala, M., Jennings, S.G. and Hoffmann, T.: Marine aerosol formation from biogenic iodine emissions, *Nature*, 417, 632-636, 2002.
- Pechtl, S., Schmitz, G. and von Glasow, R.: Modelling iodide – iodate speciation in atmospheric aerosol: Contributions of inorganic and organic iodine chemistry, *Atmos. Chem. Phys.*, 7, 1381–1393, 2007.
- Reithmeier, H., Lazarev, V., Rühm, W., Schwikowski, M., Gäggeler, H.W. and Nolte, E.: Estimate of European ¹²⁹I Releases Supported by ¹²⁹I Analysis in an Alpine Ice Core, *Environ. Sci. Technol.*, 40, 5891 -5896, 2006.

- Saiz-Lopez, A., Plane, J.M.C., McFiggans, G., Williams, P.I., Ball, S.M., Bitter, M., Jones, R.L., Hongwei, C. and Hoffmann, T.: Modelling molecular iodine emissions in a coastal marine environment: the link to new particle formation, *Atmos. Chem. Phys.*, 6, 883-895, 2006.
- Sander, R., Keene, W.C., Pszenny, A.A., Arimoto, R., Ayers, G.P., Baboukas, E., Caine, J.M., Crutzen, P.J., Duce, R.A., Hönninger, G., Huebert, B.J., Maenhaut, W., Mihalopoulos, N., Turekian, V.C. and Van Dingenen, R.: Inorganic bromine in the marine boundary layer: a critical review, *Atmos. Chem. and Phys.*, 3, 1301-1336, 2003.
- Schnell, D. and Aumann, D.C.: The origin of iodine in soil: Iodine in soils of Germany, *Chem. Erde*, 59, 69-76, 1999.
- Seto, F.Y.B. and Duce, R.A.: A laboratory study of iodine enrichment on atmospheric sea-salt particles produced by bubbles, *J. Geophys. Res.*, 77, 5339-5349, 1972.
- Slavin, G.: Derbyshire neck and iodine deficiency, *Mercian Geologist*, 16, 79-88, 2005.
- Stewart, A.: For debate: Drifting continents and endemic goiter in northern Pakistan, *British Medical Journal*, 300, 1507-1512, 1990.
- Sturges, W.T. and Barrie, L.A.: Chlorine, bromine and iodine in arctic aerosols, *Atmos. Environ.*, 22, 1179-1194, 1988.
- Vogt, R., Sander, R., von Glasow, R. and Crutzen, P.J.: Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study, *J. Atmos. Chem.*, 32, 375-395, 1999.
- von Glasow, R. and Crutzen, P.J., Tropospheric halogen chemistry. In: H.D. Holland and K.K. Turekian, Editors, *Treatise on Geochemistry*, Elsevier, 21-63, 2003.
- Whitehead, D.C.: The distribution and transformation of iodine in the environment, *Environ. Intern.*, 10, 321-339, 1984.
- WHO, Iodine status worldwide. World Health Organization, Geneva. 1-46, 2004.
- Winchester, J.W. and Duce, R.A.: The global distribution of iodine, bromine, and chlorine in marine aerosols, *Naturewissenschaften*, 54, 110-113, 1967.
- Woodcock, A.H., Duce, R.A. and Moyers, J.L.: Salt particles and raindrops in Hawaii, *J. Atmos. Sci.*, 28, 1252-1257, 1971.

Supplementary material



Sup. Fig. 1: % organically bound iodine in snow vs. altitude. Error bars represent 1σ of replicate analysis.



Sup. Fig. 2: Change in metal concentrations in snow with altitude from the northern Black Forest. All plots fitted with exponential decay functions. Error bars represent analytical precision and were calculated as 1σ of replicate analysis.

Sup. Table 1: Total iodine, iodide and organically bound iodine in snow samples from the northern Black Forest. All concentrations in nmol/l.

Sample location	Date	Altitude (masl)	Total I	I ⁻	IO ₃ ⁻	Organo-I	Unknown peak 1 Ret. 5.4 mins.	Unknown peak 2 Ret. ca 6.8 mins	Na μmol
Ottenhöfen N 48°34'06.6'' E 008°09'42.0'' Seebach	11.02.06	326	29.5	11.4	-	18	1.3	2.6	87
N 48°34'44.1'' E 008°10'13.4'' Oberseebach	11.02.06	400	38.0	9.1	-	28.8	1.5	3.0	65
N 48°34'43.7'' E 008°10'54.7'' Elsa Weg 1	11.02.06	478	37.3	9.4	-	27.9	0.9	2.9	50
N 48°34'59'' E 008°10'54.5'' Elsa Weg 2	11.02.06	560	33.5	8.7	-	24.8	1.3	3.5	47
N 48°35'03.9'' E 008°10'41.7'' Elsa Weg 3	11.02.06	597	33.3	9.8	-	23.5	1.2	2.8	48
N 48°35'13.2'' E 008°10'29'' Elsa Weg 4	11.02.06	614	32.3	9.5	-	22.9	1.1	2.7	47
N 48°35'21.8'' E 008°10'47.1'' Elsa Weg 6	12.02.06	718	18.6	6.1	-	12.5	0.6	1.7	27
N 48°35'19.3'' E 008°11'24.7'' Elsa Weg 7	12.02.06	796	19.9	6.2	-	13.6	0.7	2.0	23
N 48°35'39'' E 008°11'24.3'' Mummelsee	12.02.06	934	18.1	5.8	-	12.4	0.6	0.8	37
N 48°35'52'' E 008°12'08'' Hornisgrinde	12.02.06	1036	16.4	5.1	-	11.3	0.4	0.6	21
N 48°36'05.2'' E 008°12'03.2'' Mummelsee	12.02.06	1164	13.0	3.9	-	9.1	0.3	0.6	21
Mummelsee	26.01.06	1036	13.5	6.4	-	7.1		0.2	
Mummelsee	26.01.06	1036	15.4	7.2	-	8.1		0.6	
Mummelsee	26.01.06	1036	13.5	5.3	-	8.2		0.4	
Mummelsee	26.01.06	1036	13.7	6.8	-	6.9			
Elsa Weg 6 N 48°35'19.3'' E 008°11'24.7'' Elsa Weg 7	14/4/06	796	1.6	0.7	-	0.9		0.4	
N 48°35'39'' E 008°11'24.3'' Mummelsee	14/4/06	934	1.4	0.9	0.23	0.3		0.5	
N 48°35'52'' E 008°12'08'' Hornisgrinde	14/4/06	1036	4.9	2	0.4	2.4		1.1	
N 48°36'05.2'' E 008°12'03.2''	14/4/06	1164	2.4	1.1		1.3		0.5	

Sup. Table 2: Total bromine, bromide and organically bound bromine in snow samples from the northern Black Forest. All concentrations in nmol/l.

Sample location	Date	Altitude (masl)	Total Br	Br ⁻	Organo-Br	% org-Br
Ottenhöfen N 48°34'06.6'' E 008°09'42.0''	11.02.06	326	114.5	93.4	21.2	18
Seebach N 48°34'44.1'' E 008°10'13.4''	11.02.06	400	128.5	92.9	35.7	27
Oberseebach N 48°34'43.7'' E 008°10'54.7''	11.02.06	478	116.4	79.7	36.7	31
Elsa Weg 1 N 48°34'59'' E 008°10'54.5''	11.02.06	560	99.9	78.0	21.9	22
Elsa Weg 2 N 48°35'03.9'' E 008°10'41.7''	11.02.06	597	104.3	77.6	26.7	25
Elsa Weg 3 N 48°35'13.2'' E 008°10'29''	11.02.06	614	106.8	77.5	29.3	27
Elsa Weg 4 N 48°35'21.8'' E 008°10'47.1''	12.02.06	718	64.1	47.1	17.0	26
Elsa Weg 6 N 48°35'19.3'' E 008°11'24.7''	12.02.06	796	58.6	47.9	10.6	18
Elsa Weg 7 N 48°35'39'' E 008°11'24.3''	12.02.06	934	62.8	51.8	11.0	17
Mummelsee N 48°35'52'' E 008°12'08''	12.02.06	1036	47.6	37.4	10.1	21
Hornisgrinde N 48°36'05.2'' E 008°12'03.2''	12.02.06	1164	38.7	28.2	10.5	27
Mummelsee	26.01.06	1036	55.2	35.4	19.8	36
Mummelsee	26.01.06	1036	91.0	63.7	27.3	30
Mummelsee	26.01.06	1036	62.8	45.1	17.8	28
Mummelsee	26.01.06	1036	64.2	43.3	20.5	32
Elsa Weg 6 N 48°35'19.3'' E 008°11'24.7''	14/4/06	796	114.5	93.4	21.2	30
Elsa Weg 7 N 48°35'39'' E 008°11'24.3''	14/4/06	934	128.5	92.9	35.7	29
Mummelsee N 48°35'52'' E 008°12'08''	14/4/06	1036	116.4	79.7	36.7	30
Hornisgrinde N 48°36'05.2'' E 008°12'03.2''	14/4/06	1164	99.9	78.0	21.9	37

Sup. Table 3: Metal concentrations in snow from the northern Black Forest.

Sample location	Date	Altitude (masl)	Li nmol	V nmol	Mn nmol	Co nmol	Rb nmol	Zn nmol	As nmol	Mo nmol	Pb nmol	Ba nmol	Sb nmol	U pmol
Ottenhöfen N 48°34'06.6'' E 008°09'42.0''	11.02.06	326	17.3	28.9	158.0	1.6	8.0	959	4.1	5.0	36.9	23.3	4.4	33.6
Seebach N 48°34'44.1'' E 008°10'13.4''	11.02.06	400	17.3	36.7	176.0	1.4	6.5	692	5.2	5.9	44.3	21.8	5.4	33.6
Oberseebach N 48°34'43.7'' E 008°10'54.7''	11.02.06	478	14.4	30.8	118.5	1.1	5.1	606	4.6	4.3	38.1	16.3	4.4	21.0
Elsa Weg 1 N 48°34'59'' E 008°10'54.5''	11.02.06	560	14.4	33.0	114.7	1.0	4.9	637	4.0	4.9	43.0	16.0	4.6	25.2
Elsa Weg 2 N 48°35'03.9'' E 008°10'41.7''	11.02.06	597	10.1	29.6	100.5	0.9	4.4	587	3.7	3.6	37.0	14.0	3.5	21.0
Elsa Weg 3 N 48°35'13.2'' E 008°10'29''	11.02.06	614	14.4	29.8	111.6	1.0	4.9	613	4.8	4.3	40.2	16.7	4.1	21.0
Elsa Weg 4 N 48°35'21.8'' E 008°10'47.1''	12.02.06	718	5.8	19.4	56.2	0.6	2.9	362	2.9	2.6	22.6	8.6	2.5	12.6
Elsa Weg 6 N 48°35'19.3'' E 008°11'24.7''	12.02.06	796	5.8	18.1	46.4	0.5	3.3	362	3.0	2.6	20.1	7.6	2.1	12.6
Elsa Weg 7 N 48°35'39'' E 008°11'24.3''	12.02.06	934	4.3	17.9	46.2	0.5	3.3	372	3.0	2.5	19.9	7.6	2.1	12.6
Mummelsee N 48°35'52'' E 008°12'08''	12.02.06	1036	2.9	15.3	45.1	0.4	2.1	323	2.9	2.2	17.1	8.4	2.0	8.4
Hornisgrinde N 48°36'05.2'' E 008°12'03.2''	12.02.06	1164	2.9	11.0	34.4	0.3	1.5	275	2.3	1.6	12.9	6.4	1.7	8.4

Correlations

		Altitude (masl)	Total iodine	Iodide	Organo-I	Unknown peak 1	Unknown peak 2	Na	total_Br	Bromide	Organo-Br	Li	V	Mn	Co	Rb	Zn	As	Mo	
Altitude (masl)	Pearson Correlation	1																		
	Sig. (2-tailed)																			
	N	11																		
Total iodine	Pearson Correlation	-.880**	1																	
	Sig. (2-tailed)	.000																		
	N	11	11																	
Iodide	Pearson Correlation	-.938**	.884**	1																
	Sig. (2-tailed)	.000	.000																	
	N	11	11	11																
Organo-I	Pearson Correlation	-.815**	.988**	.800**	1															
	Sig. (2-tailed)	.002	.000	.003																
	N	11	11	11	11															
Unknown peak 1	Pearson Correlation	-.917**	.891**	.900**	.842**	1														
	Sig. (2-tailed)	.000	.000	.000	.001															
	N	11	11	11	11	11														
Unknown peak 2	Pearson Correlation	-.886**	.927**	.853**	.905**	.913**	1													
	Sig. (2-tailed)	.000	.000	.001	.000	.000														
	N	11	11	11	11	11	11													
Na	Pearson Correlation	-.871**	.738**	.902**	.647*	.840**	.667*	1												
	Sig. (2-tailed)	.000	.009	.000	.032	.001	.025													
	N	11	11	11	11	11	11	11												
total_Br	Pearson Correlation	-.941**	.969**	.940**	.930**	.923**	.885**	.865**	1											
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	.001												
	N	11	11	11	11	11	11	11	11											
Bromide	Pearson Correlation	-.955**	.932**	.964**	.874**	.950**	.875**	.919**	.984**	1										
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	.000	.000											
	N	11	11	11	11	11	11	11	11	11										
Organo-Br	Pearson Correlation	-.794**	.935**	.770**	.942**	.750**	.800**	.639*	.914**	.827**	1									
	Sig. (2-tailed)	.004	.000	.006	.000	.008	.003	.034	.000	.002										
	N	11	11	11	11	11	11	11	11	11	11									
Li	Pearson Correlation	-.936**	.916**	.923**	.867**	.932**	.888**	.891**	.962**	.965**	.838**	1								
	Sig. (2-tailed)	.000	.000	.000	.001	.000	.000	.000	.000	.000	.001									
	N	11	11	11	11	11	11	11	11	11	11	11								
V	Pearson Correlation	-.911**	.979**	.889**	.959**	.950**	.935**	.781**	.972**	.956**	.888**	.939**	1							
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	.005	.000	.000	.000	.000								
	N	11	11	11	11	11	11	11	11	11	11	11	11							
Mn	Pearson Correlation	-.917**	.886**	.892**	.839**	.931**	.813**	.921**	.952**	.957**	.825**	.969**	.920**	1						
	Sig. (2-tailed)	.000	.000	.000	.001	.000	.002	.000	.000	.000	.002	.000	.000							
	N	11	11	11	11	11	11	11	11	11	11	11	11	11						
Co	Pearson Correlation	-.945**	.821**	.916**	.748**	.905**	.774**	.967**	.922**	.954**	.739**	.951**	.864**	.975**	1					
	Sig. (2-tailed)	.000	.002	.000	.008	.000	.005	.000	.000	.000	.009	.000	.001	.000						
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11					
Rb	Pearson Correlation	-.938**	.798**	.927**	.715*	.896**	.767**	.974**	.904**	.952**	.683*	.937**	.841**	.944**	.990**	1				
	Sig. (2-tailed)	.000	.003	.000	.013	.000	.006	.000	.000	.000	.021	.000	.001	.000	.000					
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11				
Zn	Pearson Correlation	-.906**	.782**	.947**	.688*	.882**	.760**	.977**	.883**	.935**	.656*	.929**	.820**	.925**	.967**	.976**	1			
	Sig. (2-tailed)	.000	.004	.000	.019	.000	.007	.000	.000	.000	.028	.000	.002	.000	.000	.000				
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11			
As	Pearson Correlation	-.853**	.937**	.837**	.922**	.855**	.826**	.753**	.948**	.910**	.918**	.928**	.935**	.910**	.851**	.822**	.778**	1		
	Sig. (2-tailed)	.001	.000	.001	.000	.001	.002	.007	.000	.000	.000	.000	.000	.000	.001	.002	.005			
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11		
Mo	Pearson Correlation	-.918**	.915**	.874**	.882**	.957**	.876**	.864**	.951**	.959**	.817**	.974**	.962**	.974**	.939**	.917**	.888**	.932**	1	
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	.001	.000	.000	.002	.000	.000	.000	.000	.000	.000	.000		
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11
Pb	Pearson Correlation	-.897**	.972**	.903**	.945**	.948**	.940**	.782**	.964**	.951**	.876**	.948**	.992**	.911**	.854**	.835**	.835**	.928**	.954**	1
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.004	.000	.000	.000	.000	.000	.000	.000	.001	.001	.001	.000	.000	
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11
Ba	Pearson Correlation	-.909**	.850**	.915**	.786**	.912**	.785**	.948**	.932**	.950**	.776**	.969**	.885**	.988**	.982**	.961**	.963**	.886**	.954**	1
	Sig. (2-tailed)	.000	.001	.000	.004	.000	.004	.000	.000	.000	.005	.000	.000	.000	.000	.000	.000	.000	.000	
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11
Sb	Pearson Correlation	-.905**	.946**	.872**	.922**	.935**	.890**	.838**	.965**	.950**	.879**	.976**	.973**	.968**	.914**	.880**	.866**	.942**	.987**	1
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	.001	.000	.000	.000	.000	.000	.000	.000	.000	.001	.000	.000	
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11
U	Pearson Correlation	-.920**	.845**	.890**	.788**	.954**	.818**	.941**	.924**	.956**	.736**	.954**	.902**	.981**	.977**	.965**	.943**	.848**	.968**	1
	Sig. (2-tailed)	.000	.001	.000	.004	.000	.002	.000	.000	.000	.010	.000	.000	.000	.000	.000	.000	.001	.000	
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

2.3 Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to precipitation

B.S. Gilfedder¹, S. Lai², M. Petri³, H. Biester¹, T. Hoffmann²

1. *Institut für Umweltgeochemie, Neuenheimer Feld 236 69120 Heidelberg Germany*

2. *Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University, Mainz.*

3. *Bodensee-Wasserversorgung, Sipplingen Laboratory Germany*

Status: submitted *Atmospheric Chemistry and Physics* 2008

Abstract

Iodine oxides such as iodate should, theoretically, be the only stable sink species for iodine in the troposphere. However, field observations have increasingly found very little iodate and significant amounts of iodide and organically bound iodine. The aim of this study was to investigate iodine speciation, including the organic fraction, in rain, snow, and aerosols in an attempt to further clarify aqueous phase iodine chemistry. Diurnal aerosol samples were taken with a 5 stage cascade impactor and a virtual impactor (PM 2.5) from the Mace Head research station during summer 2006. Rain was collected from Australia, New Zealand, Patagonia, Germany, Ireland, and Switzerland whereas snow was obtained from Greenland, Germany, Switzerland, and New Zealand. All samples were analysed for total iodine by inductively coupled plasma mass spectrometry (ICP-MS) and speciation was facilitated by coupling an ion chromatography unit to the ICP-MS. Total iodine in the aerosols from Mace Head gave a median concentration of 50 pmol m⁻³ of which the majority was associated with the organic fraction (median day: 91 ± 7 %, night: 94 ± 6 % of total iodine). Iodide exhibited higher concentrations than iodate (median 5 % vs. 0.8 % of total iodine), and displayed significant enrichment during the day compared to the night. Interestingly, up to 5 additional, presumably anionic organic peaks were observed in all IC-ICP-MS chromatograms, composing up to 15 % of the total iodine. Organically bound iodine was also the dominant fraction in all rain and snow samples, with lesser amounts of iodide and iodate (iodate particularly low in snow). Two of the same unidentified peaks found in aerosols were also observed in precipitation from both southern and northern hemispheres, suggesting that these species are transferred from the aerosol phase into precipitation. It is suggested that organo-I is formed by reactions between HOI and organic matter derived from the ocean surface layer. This may then photolytically decompose to give iodide and the unidentified species. The data in this study show that iodine oxides are the least abundant species in rain, snow, and aerosols and therefore considerably more effort is required on aqueous phase iodine chemistry for a holistic understanding of the iodine cycle.

2.3.1 Introduction

Iodine speciation in aerosols and precipitation has been of interest recently in both atmospheric research and more applied environmental geochemistry and health. For example,

release and photolysis of iodine gases such as I_2 and CH_2I_2 followed by homogeneous nucleation of iodine oxides has been suggested as a novel processes leading to new particle formation in the marine/coastal boundary layer (O'Dowd et al., 2002; McFiggans et al., 2004; Saiz-Lopez and Plane, 2004; O'Dowd and Hoffmann, 2005; Sellegri et al., 2005; Whalley et al., 2007). If the global flux of these particles is large enough they may influence the global energy budget by scattering of incoming solar radiation. Moreover, it has also been suggested that these particle may grow large enough to form cloud condensation nuclei, and thus lead to enhanced droplet number concentrations and so further increase reflectance and scattering of incoming solar radiation (Caine, 2007). At the very least, plumes of iodine derived aerosols have been observed extending to a few hundred meters into the coastal boundary layer at Mace Head (Sellegri et al., 2005 and refs. therein). To date, the new particles are thought to form through polymerization of IO_2 dimers and to initially consist of purely oxidized forms of iodine such as I_2O_4 or I_2O_5 (McFiggans, 2005; Saunders and Plane, 2005). These species should decay to IO_3^- shortly after formation or may even be taken up as HIO_3 from the gas phase (Pechtl et al., 2007). Most models predict that iodate is the only stable iodine species in aerosols, rain and snow and that any reduced iodine species such as iodide should be oxidized (by ICl , O_3 and other highly oxidizing species) at diffusion controlled rates to I_2 , HOI and then further to IO_3^- (Vogt et al., 1999; McFiggans et al., 2000; Pechtl et al., 2006; Saiz-Lopez et al., 2006; Enami et al., 2007). Alternatively, models predict that the intermediate species such as I_2 or IBr may degas to the gas phase leaving the aerosol progressively depleted in halogens during ageing. However, field studies and more recent modeling attempts have suggested at the importance of organic iodine species in aerosols and precipitation and have also found iodine enrichment factors (relative to ocean water) in excess of 1000 (Gillfedder et al., 2007b). Moreover, Rosinski and Parungo (1966) have shown data from both field and laboratory experiments that suggest reactions between gaseous iodine (I_2) and vegetation derived VOCs (e.g. terpenes) to form ice nuclei on exposure to UV radiation and natural sunlight. Both camphor-I compounds and CH_3I were identified by mass spectrometry, although due to the rather rudimentary experimental setup it is impossible to tell if the iodine was bound to the organics in the gas phase or within the aerosols after nucleation of the organic precursors. Indeed, despite many laboratory studies showing the formation of IO_2 - IO_2 derived aerosols, little direct field evidence exists for the presence of oxidized iodine species in the particle phase. This is mostly hampered by methods for reliable speciation at low iodine concentrations and a method for sampling nucleation size aerosols.

On a more applied level, 30 % of the world's population suffers from insufficient iodine intake (de Benoist et al., 2004). This is not unilaterally confined to less developed countries

either; many of the more industrialized countries (e.g. Ireland) also have insufficient iodine intake despite iodine supplements added to salt (de Benoist et al., 2004). As such, the sources and species of natural iodine in precipitation (which is the dominant iodine contributor to soils: Fuge and Johnson, (1986) Schnell and Aumann, (1999)) are of concern to the wider population.

The aim of this communication is to demonstrate that 1) organo-I is the dominant iodine species in size segregated and PM 2.5 aerosols sampled at Mace Head, west coast Ireland, and that iodate is the least abundant species and; 2) organo-I in precipitation occurs globally and that at least one organo-I species is transferred from marine aerosols into rain and snow in both southern and northern hemispheres.

2.3.2 Methods:

2.3.2.1 Aerosol sampling

During the 2006 MAP (Marine Aerosol Production from natural sources) campaign aerosols were sampled at the Mace Head atmospheric research station using a Berner 5 stage cascade impact sampler fitted with cellulosic nitrate filter paper and housed in a protective shelter. The samples were taken on the 15, 17-20, 25, 26, and 29 of June and 4 of July and were segregated into day (8:00-20:00) and night (20:00-8:00) in the size ranges: stage 5 5.9-10 μm , stage 4 2-5.9 μm , stage 3 0.71-2 μm , stage 2 0.25-0.71 μm and stage 1 0.085-0.25 μm . Typically about 50 m³ of air were sampled per 12 hour sampling period at a flow rate of 4.5 l h⁻¹. To ensure that the results were not sampler dependent and to gain a better idea of short term temporal changes (morning, 8:00-14:00, afternoon, 14:00-20:00 and night, 20:00-8:00) we also employed a virtual impactor (PM 2.5 μm) for the 15, 17-20, 25, 26 and 29 of June and 6 of July. This was operated at a flow rate of 1.5 l h⁻¹. In addition, to test whether the filter material was influencing the concentrations and proportion of organic iodine we also took one sample from a high volume sampler (PM 10 μm) fitted with a quartz filter that had been precombusted at 500 °C for 24 h. It was operated at a nominal flow rate of 1.013 l min⁻¹. One day (15/6/06) of PM 2.5 samples were also taken offshore (North Atlantic Ocean) aboard the *Celtic Explorer* with a virtual impactor (PM 2.5 μm) during the day (8:00-20:00) and night (20:00-8:00). Back trajectories for these dates using the NOAA-HYSPLIT model (Sup. Figs. 1-9) and black carbon data from the Mace Head station (http://macehead.nuigalway.ie/map/g_database.html) indicated that on the 15th, 17th, 19th, 20th, and 29th of June clean marine air was arriving at the site. Samples on the 18th and particularly the 25th, 26th of June and 4th July were polluted. All aerosol samples were

extracted with milli-Q water by ultrasonification for 20 minutes and the liquid was subsequently filtered (0.45 μm) and analysed by the methods outlined in section 2.3.

2.3.2.2 Precipitation sampling

Rain samples were obtained from various locations from the southern and northern hemispheres: 2 samples from a rural location in Australia (late summer Barkers vale, N.S.W.), 1 sample from a coastal rural location on the north island of New Zealand (early autumn, Oakura), 4 samples from Patagonia Chile (from Biester et al., (2004) as given in Gilfedder et al., (2006)), 8 samples from Mace Head, Ireland (collected on the same dates as aerosol samples to allow a comparison between aerosol and droplet phases), 1 sample from rural East Germany (summer, Lauchhammer), 1 sample from the Black Forest Germany (spring), 26 samples from Lake Constance, Germany (Gilfedder et al., 2007b), and 2 samples from different parts of the Alps (autumn, Sedrun and summer, Interlarken), Switzerland. Note that the samples from Mace Head were collected at two locations; firstly from the atmospheric research station located near the shore and secondly from a small cottage about 200 m inland from the station. Samples were collected either directly into LDPE bottles or with a polypropylene funnel (that had previously been cleaned with Milli-Q water) draining into the sample bottle. Snow samples were collected in LDPE from Greenland (clean sector, Summit camp), Lake Constance, and the Black Forest (from Gilfedder et al., (2007a)), both Germany, the Alps (Fiescherhorn Glacier ice and hail from the mountains around Interlaken), Switzerland and Mt. Eggmont, New Zealand. Most samples from Europe were analysed within a few weeks and all samples were analysed within 2 months.

2.3.2.3 Analytics

All rain, snow and aerosol samples were filtered through 0.45 μm filters and analysed for iodine species by ion chromatography-inductively coupled plasma mass spectrometry (IC-ICP-MS) by the methods outlined in Gilfedder et al., (2007a). Total iodine was measured by normal mode ICP-MS. Due to the high total iodine concentrations in aerosol samples total iodine was diluted by a factor of 10 prior to analysis. Organically bound iodine was calculated as total I - Σ inorganic species. Unknown species identified in IC-ICP-MS chromatograms were quantified using the iodide calibration curve. This should not present a problem as all iodine is ionized to I^+ in the plasma prior to being quantified by the MS system. Total iodine and iodide calibrations were checked periodically with standard reference material BCR611, which has a recommended total iodine concentration of 9.65 $\mu\text{g l}^{-1}$ and iodide level of 9.4 $\mu\text{g l}^{-1}$. Unfortunately, there is currently no standard reference material for iodate. Concentrations were always within the standard deviation given in the certificate and deviated from the

average value by less than 10 %. Replicate analysis for three consecutive aerosol samples gave a relative standard deviation of 2.2 % for total iodine. The precision of the speciation measurement was calculated based on 15 replicates of the standard reference material over 2 months, which gave a value of 4.1 %.

2.3.3 Results

2.3.3.1 Iodine speciation in aerosols and rain from Mace Head

Total iodine levels in size-segregated aerosols were relatively consistent over the sampling period (median 50 pmol m⁻³), except for on the 15 of June, when concentrations were considerably higher (up to 532 pmol m⁻³) than on all other sampling dates (Figure 1). Organically bound iodine was the dominant species in the aerosol samples from Mace Head (median 41 pmol m⁻³, range 3.71-509 pmol m⁻³), accounting for 67-95 % (median 91 ± 7 %) of the total iodine during the day and 70-98 % (median 94 ± 6 %) of the total iodine during the night (Figure 1).

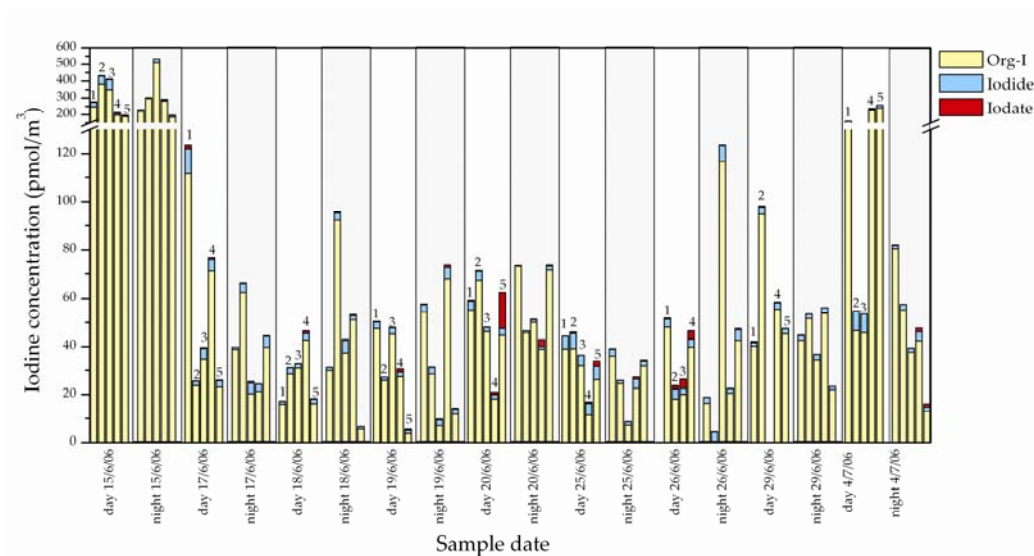


Figure 1: Total iodine, organically bound iodine, iodide, and iodate concentrations in size-segregated aerosols from Mace Head research station. Numbers in graph represent the different impactor stages and the grey shading shows nighttime sampling.

Iodide was the most abundant inorganic aerosol species (median 2.5 pmol m⁻³, range 0.3-58 pmol m⁻³), except for a few isolated cases in the largest size modes, where iodate and iodide concentrations were about equal. Iodate concentrations ranged from below detection to 15 pmol m⁻³, with a median of 0.8 % and maximum of 24 % of the total iodine. Figure 2 presents the night to day ratio of iodine concentrations in the size-segregated aerosols to highlight diurnal trends in the data. Values above one indicate enrichment during the night relative to the previous day, whereas values below one demonstrate and enrichment during the day

relative to the night. Each iodine species in Figure 2 was subject to a Chi-square (χ^2) statistical test with Yates correction for continuity in an attempt to ascertain whether day-night differences in iodine speciation were significant. This test ignores the magnitude of the enrichments, and treats the data nominally, being either 'day' or 'night' enriched. Data that showed neither enrichment during the day or night (i.e. fell onto the '1' line) was excluded from the test. The results demonstrated that there was no significant difference between the numbers of observations being enriched during the night compared to the day for all species except for iodide ($p > 0.05$). For iodide the number of observations of daytime enrichment was significantly higher than the number of observations falling into the night enriched category ($p < 0.05$). There was no noticeable dependence of iodine species on aerosol size classes unless the data was normalized by the logarithm of impactor size ranges (i.e. by channel size; concentration/dlogDp). Such transformations allow a more representative comparison between the impactor stages and, as shown in Figure 3, is given here as the average for each aerosol size class over the study period. After normalization, there was still very little difference between the different aerosol size class for total iodine, organo-I, and iodide (Figure 3). Iodate appeared to be concentrated in the largest size fractions during both day (67 % of iodate in the $>2 \mu\text{m}$ fraction) and night (79 % of iodate in the $>2\mu\text{m}$ fraction) in agreement with the data in Baker, (2005). Figure 3 also shows that, on average, iodide levels were higher during the day than during the night, except for on impactor stage 4.

In the PM 2.5 samples total iodine concentration were considerably higher on the 15th of June compared to all other sampling days, as observed in the sized segregated samples (Figure 4). Also, the concentrations were considerably higher with the Virtual impactor than with the cascade impactor, with a maximum of 1534 pmol m^{-3} on the morning of the 15th. The PM 2.5 results also displayed a pronounced minima in total iodine levels during the night in most cases, while there were no notable systematic differences between morning and afternoon samples. Organically bound iodine was the dominant species accounting for 69-96 % of the total iodine and iodate was the least abundant, with a median and maximum of 1.24 % and 6 % respectively. The offshore PM 2.5 samples from the 15th of June contained significantly lower iodine levels (day- 410 pmol m^{-3} , night 561 pmol m^{-3}) compared to the Mace Head station samples collected on the same day (Figure 4) but closely resembled the station data between 17-29 of July. This strongly suggests that the coastal environment was the source of the excess iodine in the station samples observed on the 15th and that the other samples more closely represented background marine conditions. This is supported by the diurnal iodine data from Rancher and Kritz, (1980), which showed very similar iodine concentrations to those presented here, despite being taken during clean marine conditions aboard the R/V

Capricorne over the Atlantic Ocean. Organically bound iodine was again the dominant iodine component in both offshore samples (day 92 %, night 91 % of the total iodine) followed by iodide (day 28 pmol m⁻³, night 49 pmol m⁻³) and iodate (day 1.9 pmol m⁻³, night 1.6 pmol m⁻³).

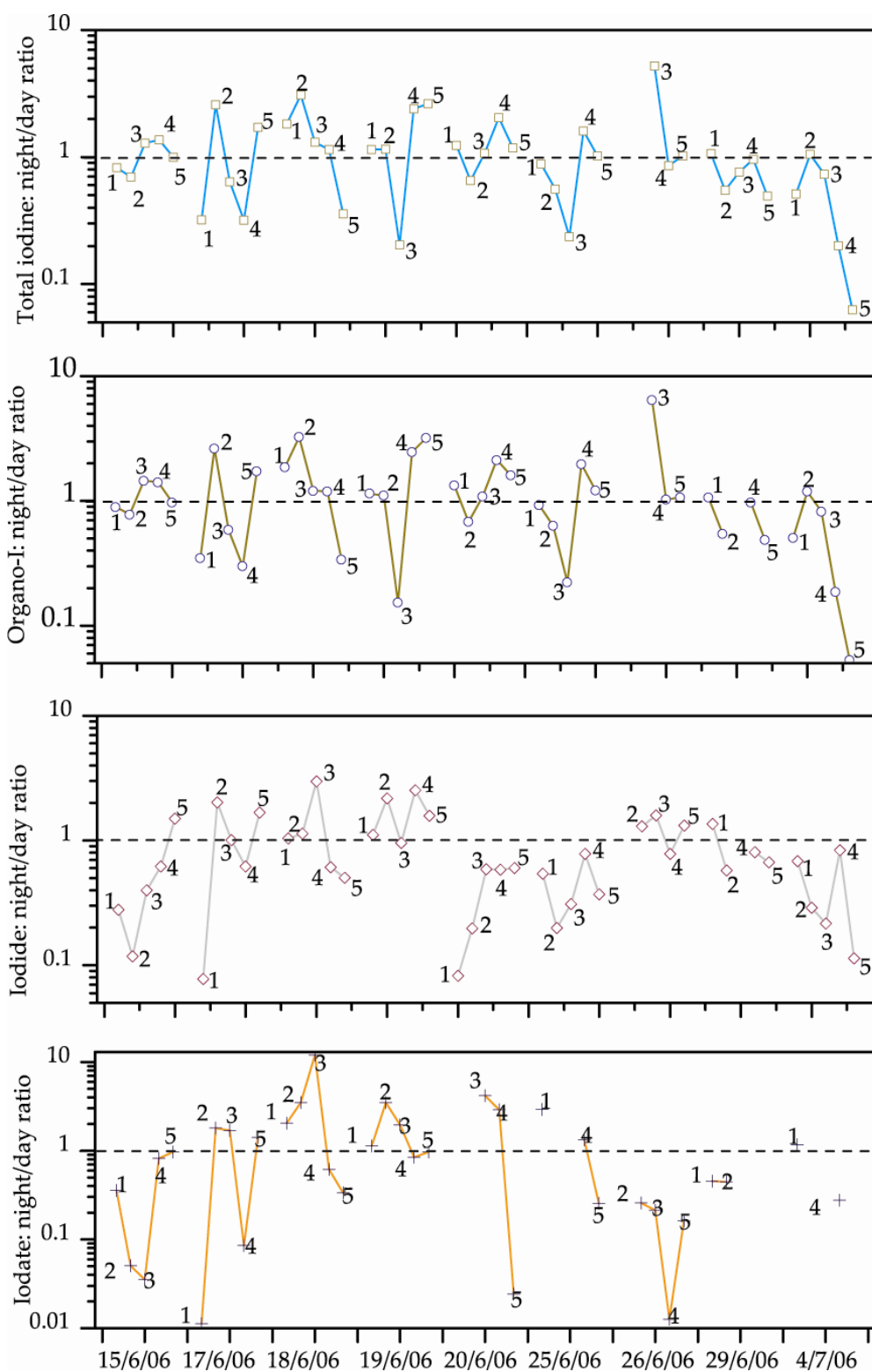


Figure 2: Size segregated iodine concentrations from nighttime samples divided by iodine concentrations in samples from the previous day. Numbers indicated impactor stage (i.e. aerosol size fraction) and dotted line shows 1:1 relationship between day and night. Note that where no data exists either measurement was not possible or concentrations were below the detection limit.

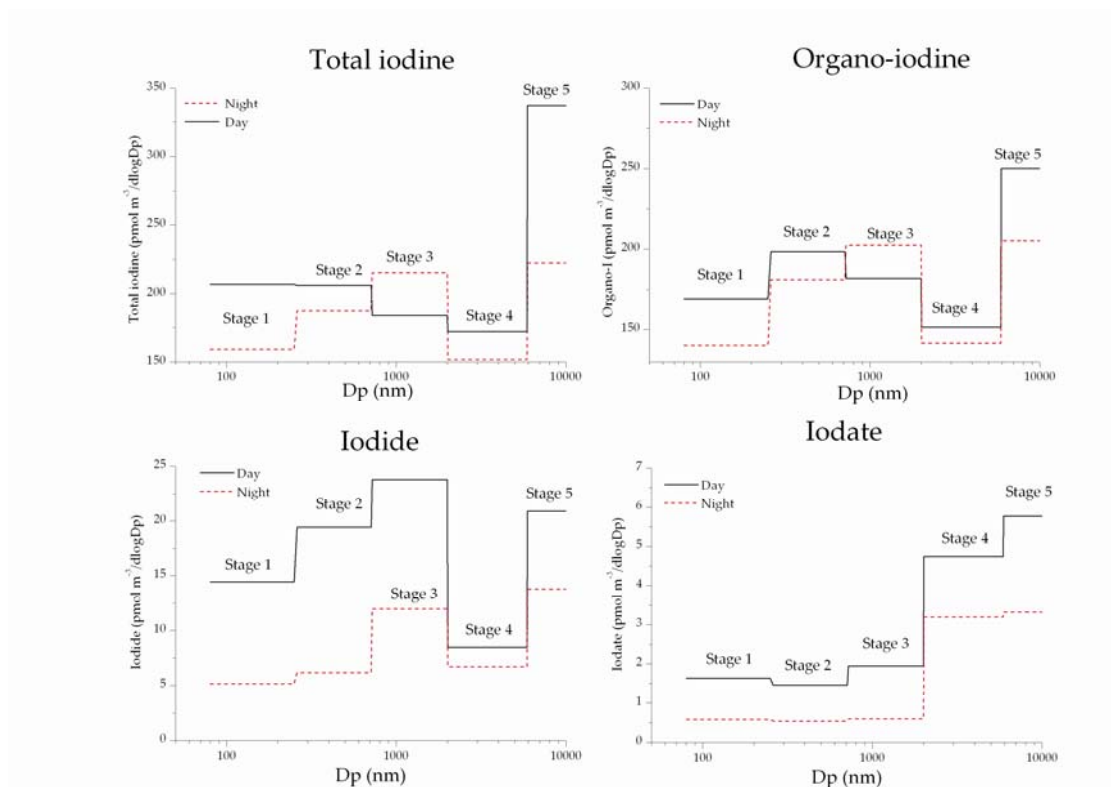


Figure 3: Normalized (dlogDp) average iodine speciation in size segregated aerosols. Each stage is averaged over the respective impactor stages and the study period.

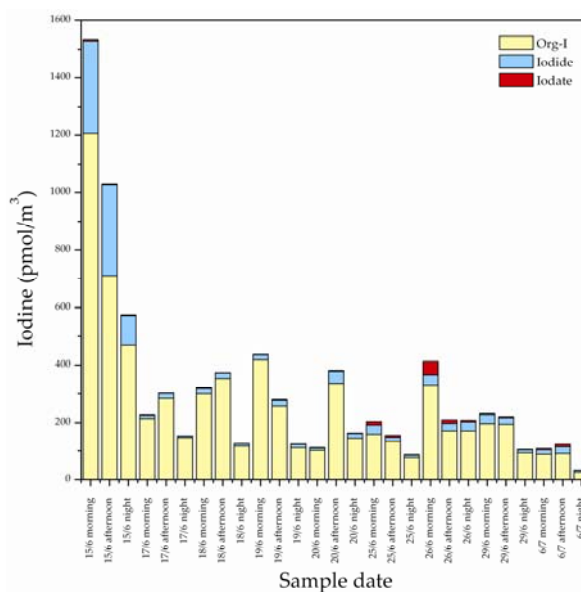


Figure 4: Organically bound iodine, iodide and iodate concentrations in aerosols collected with a Virtual impactor (PM 2.5) during the morning (8:00-14:00), afternoon (14:00-20:00) and night (20:00-8:00).

In addition to the organically bound iodine calculated by the mass balance approach described above, the IC-ICP-MS chromatograms also contained up to 5 peaks in addition to the inorganic iodide and iodate species (Figure 5 and 6). These peaks were observed in size-segregated samples, and PM 2.5 samples from the station and offshore as well as the PM 10 sample (Supplementary material Figures 10 and 11). Other than the peak eluting shortly after

iodate (retention time ca. 4 min. 40 sec; note that the exact retention time depends on age of the column and to a lesser extent ambient conditions such as room temperature) which corresponded to an iodoacetic acid standard, all of these additional peaks remain unidentified. The iodoacetic acid concentrations had a median value of 0.2 pmol m^{-3} ($<0.03\text{-}1.66 \text{ pmol m}^{-3}$; $n=30$) during the day and 0.1 pmol m^{-3} ($<0.03\text{-}0.3 \text{ pmol m}^{-3}$; $n=25$) during the night. Unfortunately there were not enough consecutive data points to allow any thorough investigation of diurnal or aerosol size related trends. To date we have injected all commercially available standards such as iodoacetic acid, diiodoacetic acid, I_3^- , iodopropionic acid, and a range of aromatic iodine compounds into the IC-ICP-MS system. Unfortunately none of these matched the unidentified peaks. However, these species must be organic (due to the instability of all inorganic species other than iodide and iodate), and anionic as they are efficiently separated by the anion exchange column. The largest of these unknown species (termed peak (p) 4; elution time ca. 7-8 min.) was often even more abundant than iodate. There were also significant correlations between the unknown peaks and iodide during the day, although this tended to collapse during the night. Correlations with total iodine, organo-I and iodate were much weaker (Figure 7).

Organically bound iodine was also the major fraction in the rain samples from Mace Head station and the cottage (Table 1). However, the organically bound iodine in rain consistently composed a lower proportion of the total iodine compared to the aerosol samples and generally had a larger proportion of iodate. In fact, in some of the rain samples iodate was at a similar, or slightly higher, concentration than iodide. This is in very good agreement with inorganic iodine speciation measurements in rainfall from the North Sea region, analysed by electrochemistry (Campos et al., 1996), and rainfall from west England measured by photometry (Truesdale and Jones, 1996). This is further confirmation that our speciation technique is accurately recording the iodide and iodate levels. Interestingly, the largest of the unknown compounds (p4) observed in the aerosol chromatograms was also consistently found in the Mace Head rain chromatograms (Figure 8).

Table 1: Total iodine concentrations and speciation in rainfall from the Mace Head station and Mace Head cottage. All concentrations in nmol l^{-1} except where indicated.

Sample location	Sample date	Total iodine	Iodide	Iodate	Organo-I	% organo-I
Mace Head station	17-18/6/06	19.7	3	3.4	13.3	67
Mace Head cottage	17-18/6/06	20.5	2.3	3.7	14.5	70
Mace Head station	19-20/6/06	24.4	5	3.7	15.8	64
Mace Head cottage	19-20/6/06	33.1	8.7	4.7	19.7	60
Mace Head station*	26/6/06	37	6.8	4.2	26	70
Mace Head cottage	29/6/06	30.7	5.8	3.9	20.9	68
Mace Head station	8/7/06	47.3	6.4	1.72	39.2	83
Mace Head cottage	8/7/06	18.1	4.3	1.8	12.0	66

* taken over a 4 hour rain period. + Very old snow sampled about halfway up the cone of the dormant Mt. Eggmont volcano.

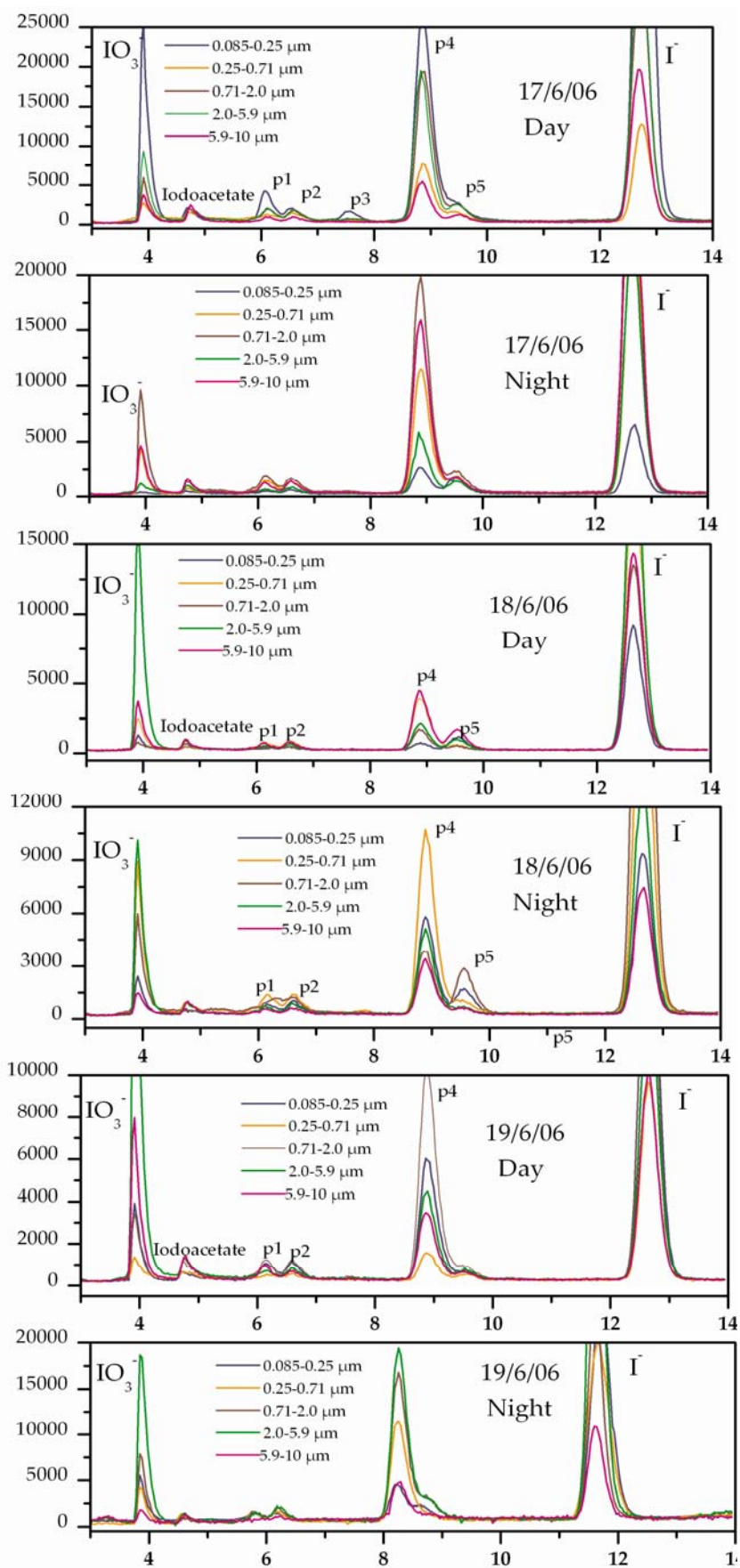


Figure 5: IC-ICP-MS speciation chromatograms of aerosols from Mace Head 17-19 of June 2006. p1 to p5 are unidentified peaks 1 to peak 5.

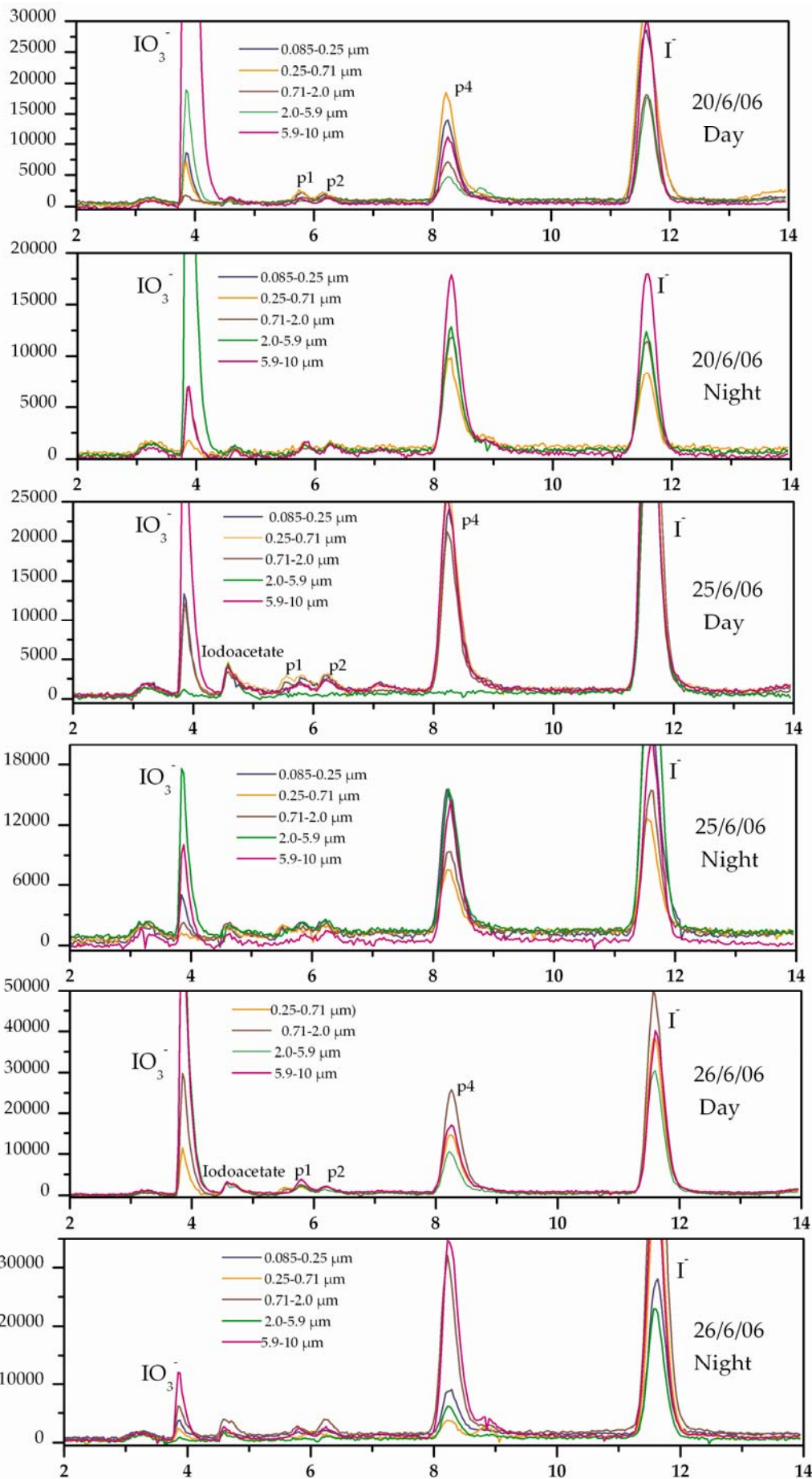


Figure 6: IC-ICP-MS chromatograms of iodine speciation in aerosols in from Mace Head.

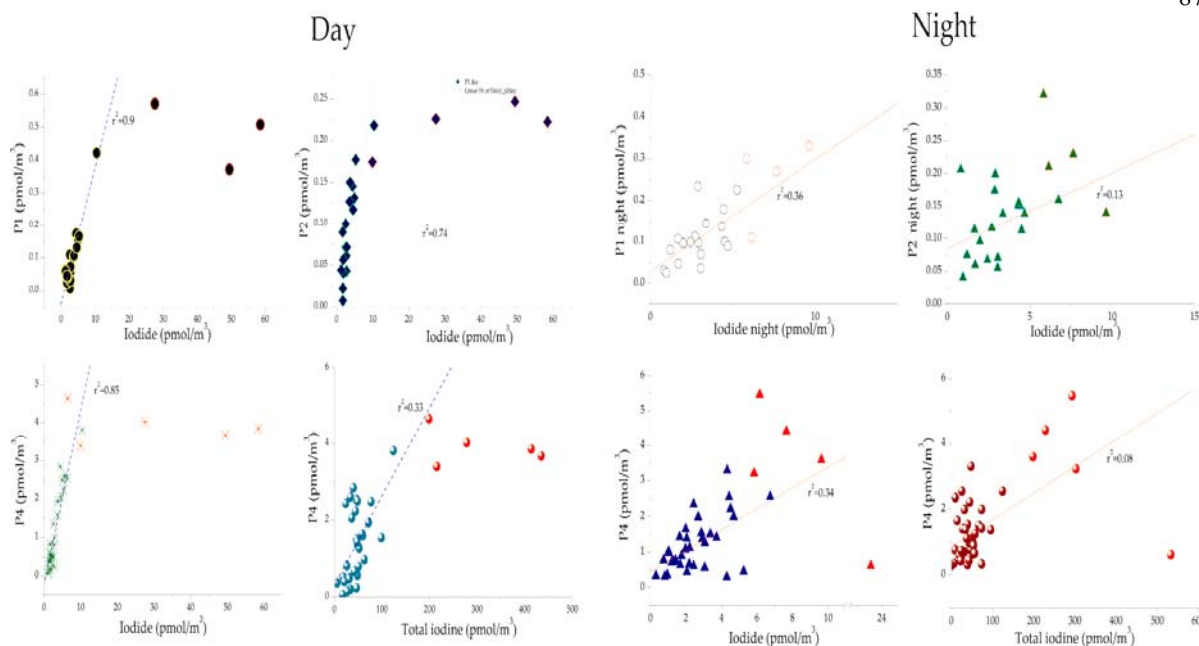


Figure 7: Correlations between the unknown peaks and iodide and total iodine. The points outlined in red are from the 15th of June and are not included in the correlations due to suspected coast influence.

2.3.3.2 Iodine speciation in rain and snow samples

Iodine concentrations in rain and snow samples from both northern and southern hemispheres were surprisingly similar given the different environments from which they were taken (Tables 2 and 3). As would be expected, the highest average concentrations were observed near the coast (e.g. Mace Head and Oakura). However, total iodine levels further inland, such as at Lake Constance, often displayed similar concentrations to locations directly adjacent to the coast. As such, there is no evidence for a strong (if any) iodine concentration gradient between the ocean and the terrestrial environment. This is at least partially supported by recent work that has found significant fluxes of methyl iodide from a number of terrestrial environments (Keppler et al., 2000; Manley et al., 2007; Sive et al., 2007). In addition, the relative uniformity observed in rain fall between the locations (see also (Krupp and Aumann, (1999)) could also be related to rapid transport of precipitation and aerosols inland from the coast. The lowest iodine concentrations in snow were observed at high altitudes, such as at the Summit camp Greenland (3200 masl), the Swiss Alps and higher parts of the Black Forest; in agreement with the exponential decrease in iodine levels with increasing altitude found by Gilfedder et al., (2007a).

Table 2: Total iodine and iodine species levels in rain from northern and southern hemispheres. All concentrations in nmol l^{-1} except where indicated.

Sample Location	Total iodine	Iodide	Iodate	Org-I	%-Org-I
Lake Constance*	11± 6.7	4.1 ± 2.6	1.3 ± 0.86	7.2 ± 4.6	54
S. Germany (n=26)					
Lauchhammer		2	0.3		
E. Germany (n=1)					
Sedrun	10.1	4.1	0.17	5.8	56
Swiss Alps (n=1)					
Oakura	13.7	2.6	1.8	8.7	63
New Zealand (n=1)					
Barkers vale	5.2	1.8	0.47	3	58
E. Australia (n=2)					
Patagonia	4.02	2.7	<0.8	1.34	33
Chile (n=2)					

* Some of this data has been given in Gilfedder et al., (2007b).

As observed in Mace Head rainfall, organically bound iodine in rain and snow from both northern and southern hemispheres was the dominant iodine species in most samples, generally accounting for over 50 % but up to 80 % of the total iodine (Tables 2 and 3). In all continental rain and particularly in the snow samples, iodate was the least abundant species, often falling below the detection limit of the method. Also, iodate levels were always higher in coastal samples than further inland. The same unidentified species described above for Mace Head rain and aerosol samples (p4) was also found in most of the rain and snow samples from both northern and southern hemisphere locations (Figure 9). In particular, the largest peak (p4) observed in aerosols from Mace Head could be traced directly from the aerosols into the rain (Figure 8). As p4 was also found in rain and snow samples at the other sampling locations, it also seems at least plausible that this unidentified species is also present in the global aerosol population.

Table 3: Total iodine and iodine species levels in snow from northern and southern hemispheres. All concentrations in nmol l^{-1} except where indicated.

Sample Location	Total iodine	Iodide	Iodate	Org-I	%-Org-I
Summit	4.02 ± 0.2	0.42 ± 0.24	<0.2	3.53 ± 0.42	88
Greenland (n=6)					
Lake Constance*	5.3 ± 2	2.7 ± 1	0.4 ± 0.2	2.6 ± 1.2	48
Germany (n=16)					
Black Forest altitude profile#	18.7	5.7	0.4	12.6	72
Germany (n=19)					
Fiescherhorn glacier	4.04 ± 1.7	1.4 ± 0.1	<0.2	2.6 ± 0.8	68
Switzerland (n=3)					
Alps Hail	1.02	0.55	<0.2	0.47	46
Switzerland (n=1)					
Mt. Eggmont ⁺	0.9	0.31	0.46	0.09	10
New Zealand (n=1)					

*Some of this data has been given in Gilfedder et al., (2007b).

No standard deviation given because concentrations decrease exponentially with increasing altitude as discussed in Gilfedder et al., (2007a).

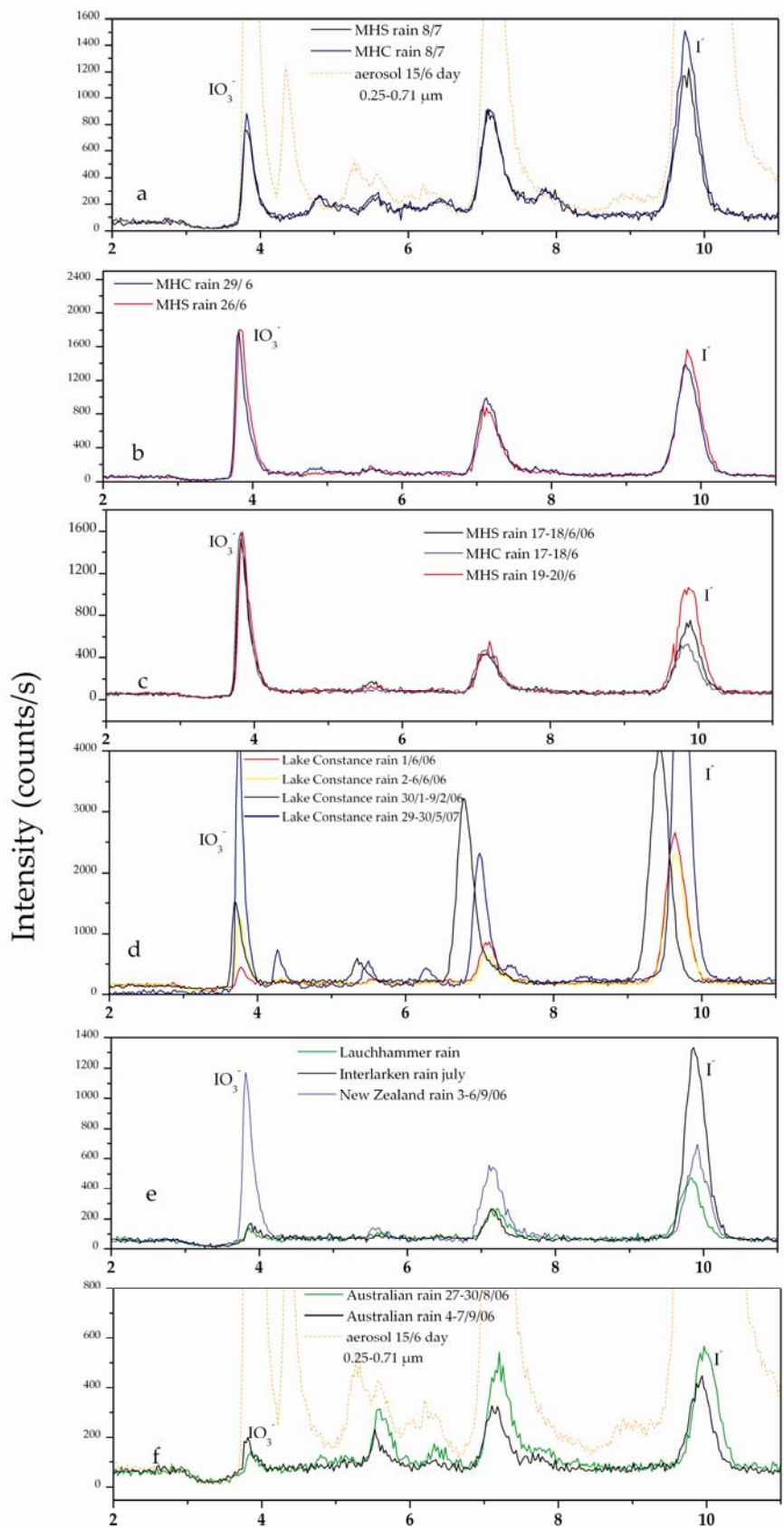


Figure 8: IC-ICP-MS chromatograms of rain samples from the southern and northern hemispheres. MHS is samples from Mace Head Station and MHC is samples from Mace Head Cottage. Note that in part (a) and (f) Mace Head aerosol sample 0.25-0.71 μm from the 15/6/06 is overlaid for a comparison between aerosol and rain speciation.

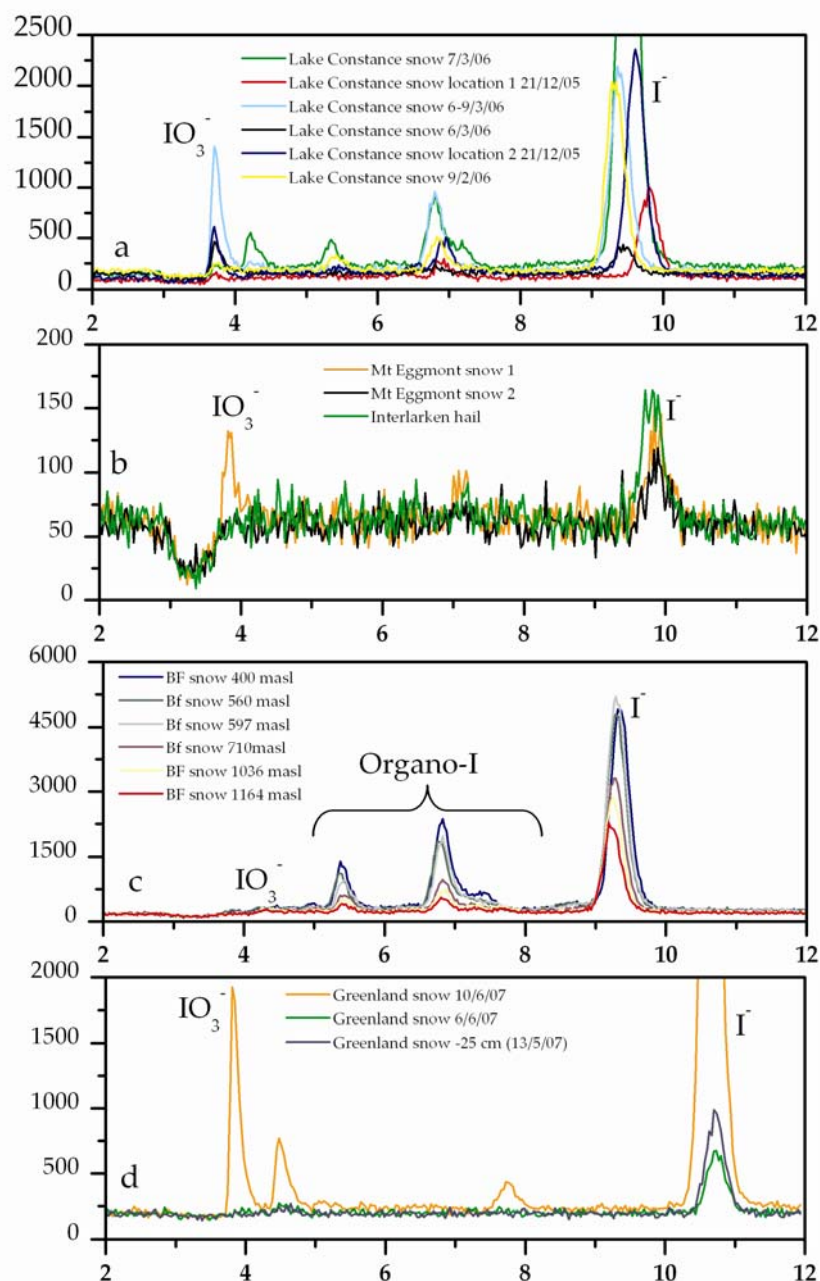


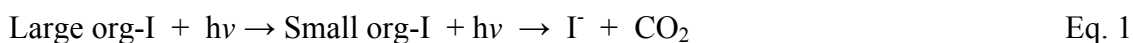
Figure 9: IC-ICP-MS chromatograms of snow samples from different locations around the world. Lake Constance is in southern Germany, Mt. Eggmont is on the west coast of the north island of New Zealand, Interlaken is a sample taken from the mountains surrounding the city of Interlaken, Swiss Alps, Bf is snow from the Black Forest Germany.

2.3.4 Discussion

The current understanding of iodine cycling in the atmosphere states that the majority of gaseous iodine is taken up, or nucleates, as iodine oxides such as HIO_3 or I_2O_5 . Theoretically, iodine oxide should be a stable sink species for iodine and thus removed from further cycling reactions in the atmosphere. While such mechanisms have traditionally been implemented in models, it is obvious from the field results presented here and elsewhere that iodate is often the least abundant species in rain, snow and aerosols (Baker et al., 2000; Baker et al., 2001;

Baker, 2004, 2005; Gilfedder et al., 2007b, a). Recent modeling studies have attempted to implement some simple organic-iodine reactions in an attempt to reconcile field data with theoretical calculations (Pechtl et al., 2007). However, even these simplified schemes are severely limited by a lack of structural identification of the iodoorganic compounds, kinetic data and indeed even if organically bound iodine is a global phenomena. The data in Baker, (2005) has, to a large degree, shown that organically bound iodine is of global importance, but other studies using complementary methods are obviously required to add weight to Baker's findings.

The data presented here shows that organically bound iodine is the most abundant species in aerosols sampled at Mace Head. In addition to the calculated organic iodine fraction (i.e. total – inorganic species) we also observe unidentified anionic iodine species in IC-ICP-MS chromatograms that can only be organic compounds. Although the largest of these species only made up, at maximum, 10-15 % of the total iodine, these species provide direct evidence that organic iodine exists in the aerosols. This is further shown by the tentative identification of low concentrations of iodoacetic acid. The unidentified peaks are most likely anionic organic iodine species of low molecular weight, as they are efficiently separated by the anion exchange resin which was initially developed by Dionex for separation of highly polarizable anions. It is thought that these species are formed by oxidative and/or photolytic decomposition of organic-iodine molecules of high molecular weight, such as iodinated marine gels or colloids and their decomposition products, observed globally in submicron aerosols by Leck and Bigg, (2005), Leck and Bigg,(2007) and Bigg, (2007). These gels are transferred into the atmosphere by bubble bursting and have been observed by microscopy at less than 50 nm sizes. Marine gels decompose both photolytically and by acidification (Chin et al., 1998; Orellana and Verdugo, 2003). For example:

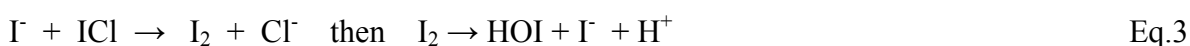


This very general reaction has been shown to occur in the marine environment, with iodide production rates on the order of 12-30 nM m² kW⁻¹ h⁻¹ (Wong and Cheng, 2001). Moreover, Eq.1 is further suggested by the number of observations of iodide enrichment being significantly higher during the day compared to the night. Some caution must be used in extrapolating rate constants from the marine environment however, as both chemical and physical conditions are vastly different to aerosols. Iodine bound to the organic molecules in the aerosols and precipitation must originate from the gas phase rather than via bubble bursting, as enrichment factors relative to ocean water are consistently higher than 1000 and

up to 10 000 (Duce et al., 1965; Moyers and Duce, 1972; Rancher and Kritz, 1980; Sturges and Barrie, 1988). In contrast, bubble bursting can only produce, at maximum, enrichment factors of ~50 (Seto and Duce, 1972). If iodine is taken up by aerosols as iodine oxides, as currently thought, it must be rapidly reduced to species such as Γ^- and HOI. Until recently there has been no mechanism for the reduction of iodate in the atmosphere. However, Pechtl et al., (2007) have recently proposed a reaction which may be able to fulfill this function:



Alternatively to Eq.2 the organic matter from the surface layer of the ocean may possess sufficient reductive potential to reduce the iodate to more reactive intermediate species, although this remains to be seen. According to the modeling work of Pechtl et al., (2007) HOI will also be formed by oxidation of iodide at diffusion controlled rates (i.e. very fast). For example:



In either case, it is most likely that it is HOI which is responsible for iodination of organic matter, as it is highly electrophilic. HOI has a strong affinity for carbon bonds, and conjugated double bonds in particular. It could be expected that the marine gels, derived from spontaneous polymerization of marine DOM in the ocean microlayer and tends to be concentrated in submicron particles by the bubble bursting process (Chin et al., 1998; O'Dowd et al., 2004), are an ideal substrate for iodination. For example,



In this reaction iodine abstracts a hydrogen atom from the carbon substrate. As an alternative to Eq. 1, the HOI may also react with small organics to form the iodoacetic acid and the other unknown compounds observed in the chromatograms. It is envisioned that the reaction between iodine and organics is a highly non-linear reaction, as the HOI would have a preference for unsaturated bonds. Unsaturated bonds are particularly prone to oxidation (by e.g. O_3 , OH or even XO), and thus the most optimal halogenation sites are expected to decrease with time. It is also feasible that once there is no, or few, available halogenation sites reduction of HOI by organic matter may play a role in maintaining iodide concentrations as implied in the reaction scheme of Pechtl et al., (2007). For example,



One interesting implication of the combination of Eq. 1, Eq. 3, Eq.4 and Eq.5 is that iodine may oscillate between iodide and organic iodine and escape both degassing from the aerosols and oxidation to higher valence states. Interestingly, this may also increase the rate of Eq. 2, which is limited by the iodide concentrations in the aerosols (Pechtl et al., 2007). Obviously, such hypothesis depends on the as yet unknown rates of Eq. 1, Eq.4 and Eq.5. Indeed, as just mentioned, the rate of Eq. 4 may change with time depending on the organic substrate characteristics and reduction potential. Also, Eq.1 is dependent on solar radiation and therefore should not be active during the night, suggesting that a diurnal cycle should be observed in the day-night data.

This ties into the diurnal sampling at Mace Head, where we attempted to identify difference in speciation during day and night, but unfortunately no strong difference was observed except for iodide. There may be two reasons for this, and the lack of an obvious cycle does not automatically render the first step of Eq. 1 invalid. Firstly, the samples were all taken on rainy days, as the primary aim at the outset of the experiment was to trace iodine species from the aerosol phase into the droplet phase. Such conditions would not be conducive to a robust testing of Eq. 1. Secondly, we have only measured the soluble organic iodine, whereas the majority of organic matter in submicron aerosols from Mace Head is insoluble (O'Dowd et al., 2004). As such, any temporal and/or diurnal trends in the data may be obscured by the extraction method which may only sample a small portion of the organic iodine. For example, we may only be sampling the second step in Eq. 1, where the largest of the insoluble organic matter has been partially oxidized to give more soluble, although still relatively large, compounds. Future studies focused on the diurnal cycling of iodine should choose days with high solar intensities and analyze the total iodine in the samples in addition to the water-soluble iodine to maximize the possibility of observing the iodination-deiodination mechanism.

So far we have only considered iodine-organic interactions in the aqueous/particle phase. While there have been limited studies on interactions between halogens and organics in the gas phase it is a worthy area of future research. For example, Toyota et al., (2004) have found that up to 20 % of atmospheric Br may end up as organo-Br formed through gas phase reactions between gaseous Br radicals and simple organics (up to C₃ hydrocarbons). Also, as mentioned in the introduction, Rosinski and Parungo, (1966) showed that iodine and biogenic gases react (forming iodoorganics as observed by mass spectrometry) to decrease the freezing temperature of ice nuclei. Moreover, chamber studies with brown macroalgae *Drwillaea*

potatorum at Cape Grim Australia found that particles produced on exposure to ozone and light were only stable in xylene, suggestive on an organic aromatic species (Cainey et al., 2007); a finding quite different to that observed in chamber experiments in the UK by McFiggans et al., (2004). Nucleation of an organic iodine species would still be consistent with the low solubility of 8 nm size aerosols found with a UF-TDMA by Väkevä et al., (2002). Therefore, while iodine oxide nucleation is still the most plausible mechanism for the large nucleation bursts observed at Mace Head (given the rather robust laboratory data of McFiggans et al., (2004) and fast kinetics of the IO-IO reaction) it would still be useful to run some chamber studies on iodine-organic interactions in the gas phase.

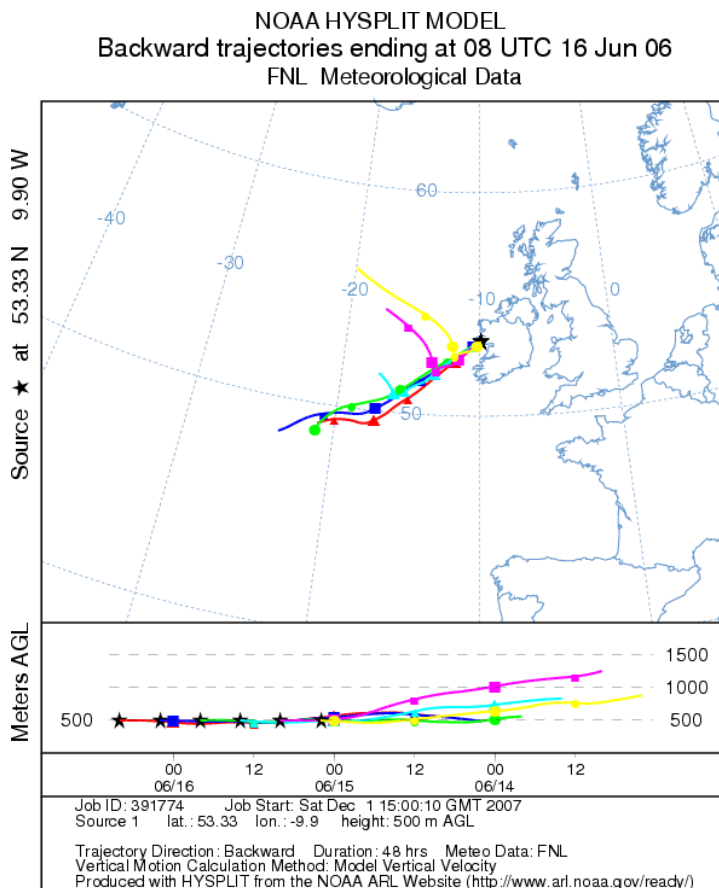
2.3.5 Conclusions

Atmospheric iodine chemistry is of increasing interest due to the nucleation of iodine gases to form new nucleation sized aerosols. These aerosols are supposedly composed of iodine oxide, although, as shown here iodine oxides are the least abundant species in accumulation and coarse mode aerosols, rain and snow with organic iodine species being dominant species. Up to five organic anionic species can be observed in the IC-ICP-MS chromatograms, but except for iodoacetic acid, remain unidentified. The most important consequence of the organo-I in the aerosols is probably by effecting the residence time of iodine within the particles, in particular by retarding iodine release to the gas phase (thus possibly decreasing ozone destruction). Organo-I may also facilitate iodine buildup in aerosols and rain to enrichment factors greater than 1000. While it is most likely that organo-I forms by aqueous phase chemistry in the aerosol, it would be useful for future laboratory based studies to investigate the possibility of iodine-organic reactions in the gas phase and subsequent condensation as an alternative to the IO₂-IO₂ nucleation hypothesis.

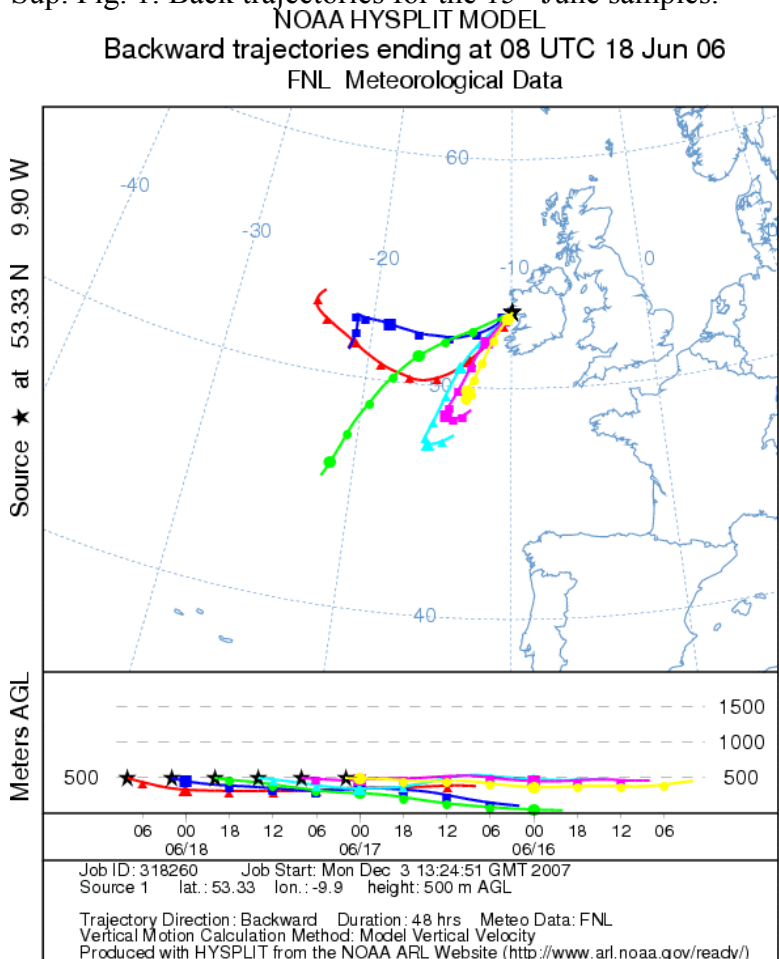
Acknowledgements

We would like to thank Joele Bauxmann and Katja Seitz for taking the Mace Head rain samples, Roland von Glasow and Matthias Piot for the snow samples from Greenland and Fred M^cgregor for the rain sample from New Zealand. BSG would like to thank Roland von Glasow and Alex Baker for very stimulating discussions about atmospheric iodine chemistry during an invited visit to UEA. This project was supported by DFG grant to H. Biester under contract No. BI-734/4-5.

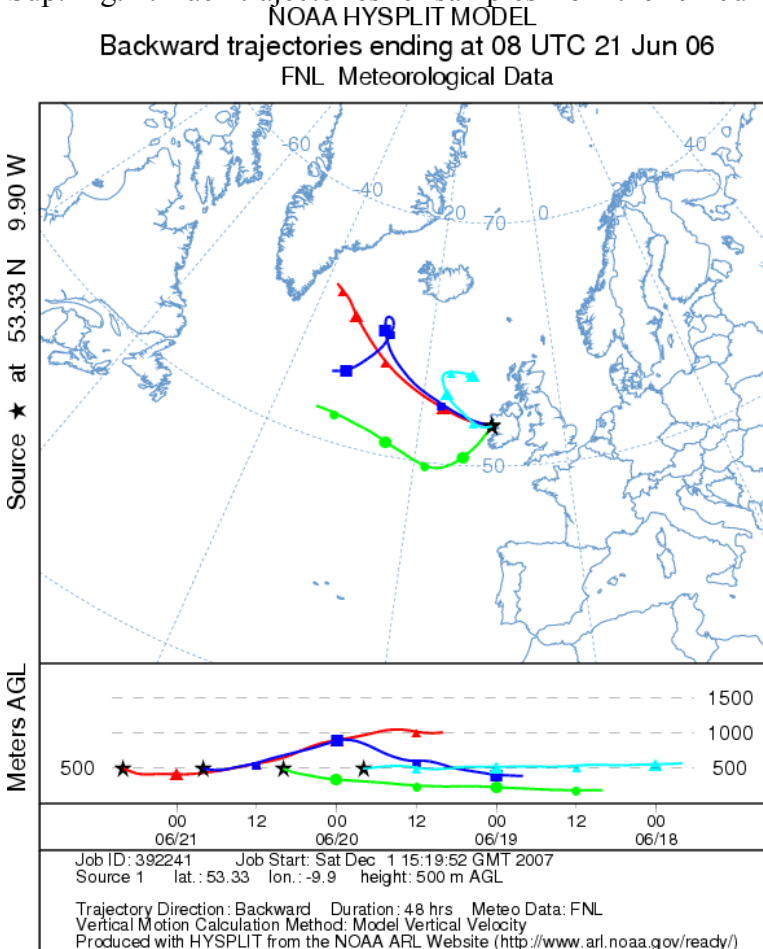
Supplementary material



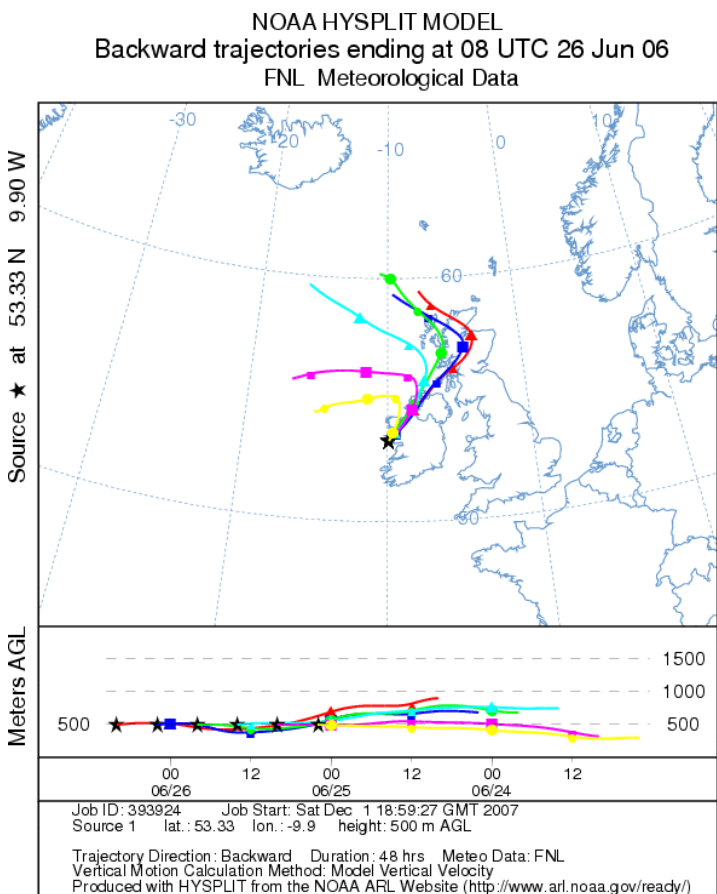
Sup. Fig. 1: Back trajectories for the 15th June samples.



Sup. Fig. 4: Back trajectories for samples from the 19th June.

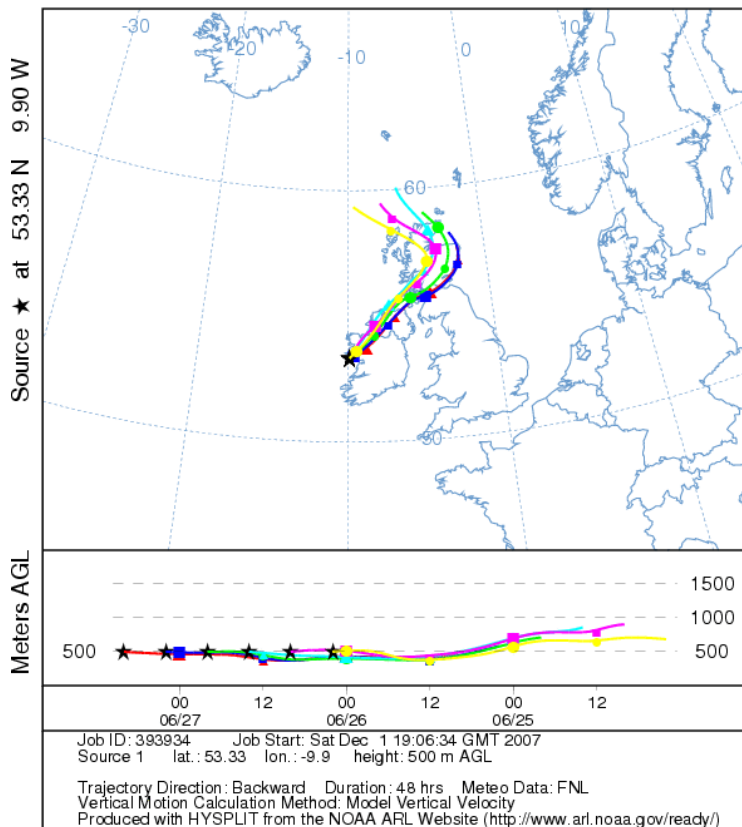


Sup. Fig. 5: Back trajectories for samples from the 20th June.



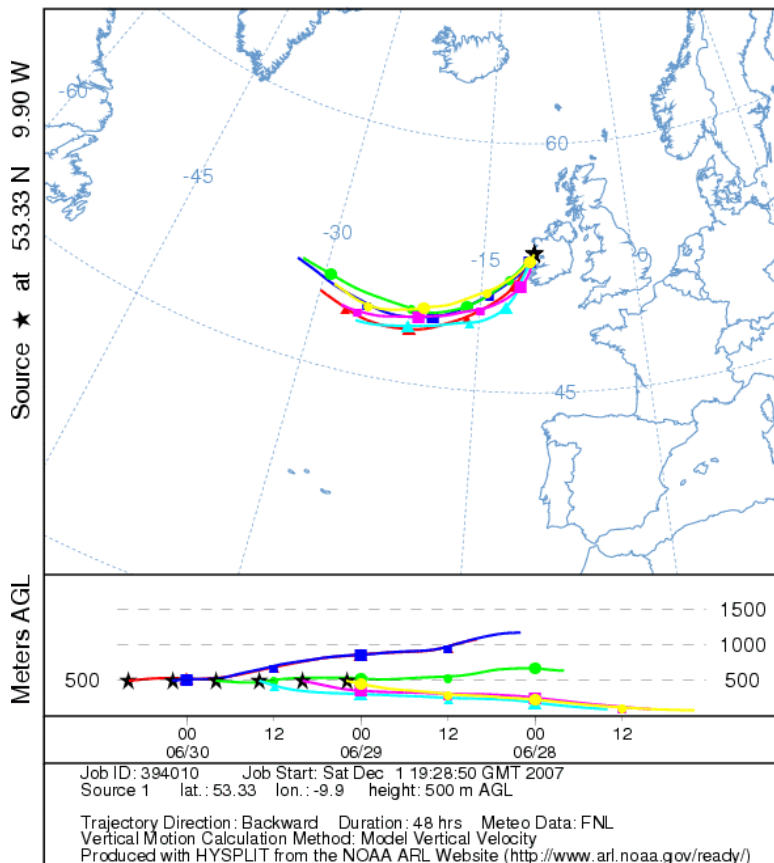
Sup. Fig. 6: Back trajectories for samples taken on the 25th June.

NOAA HYSPLIT MODEL
 Backward trajectories ending at 08 UTC 27 Jun 06
 FNL Meteorological Data



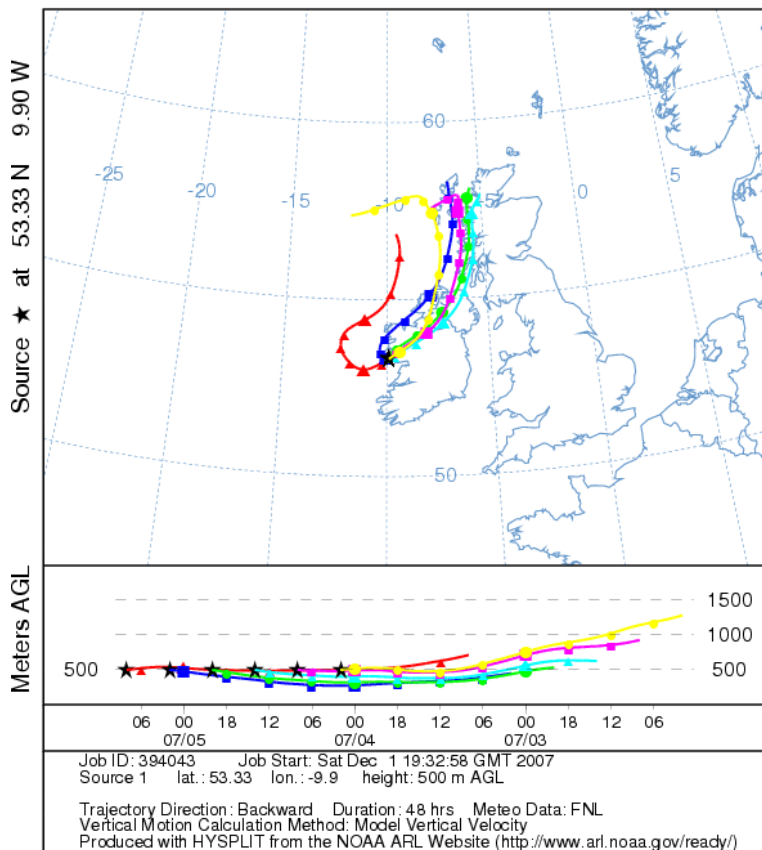
Sup. Fig. 7: Back trajectories for samples taken on the 26th June.

NOAA HYSPLIT MODEL
 Backward trajectories ending at 08 UTC 30 Jun 06
 FNL Meteorological Data

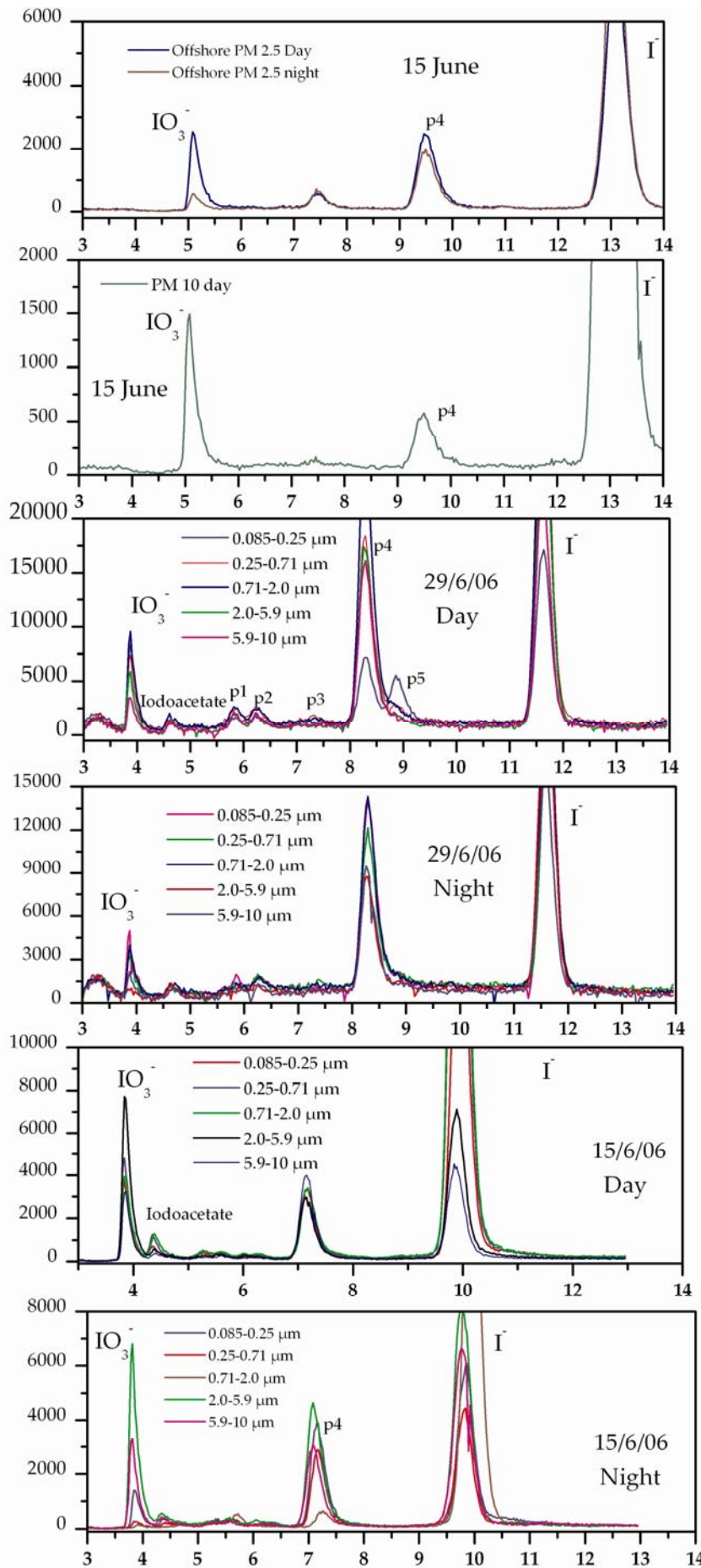


Sup. Fig. 8: Back trajectories for samples taken on the 29th June.

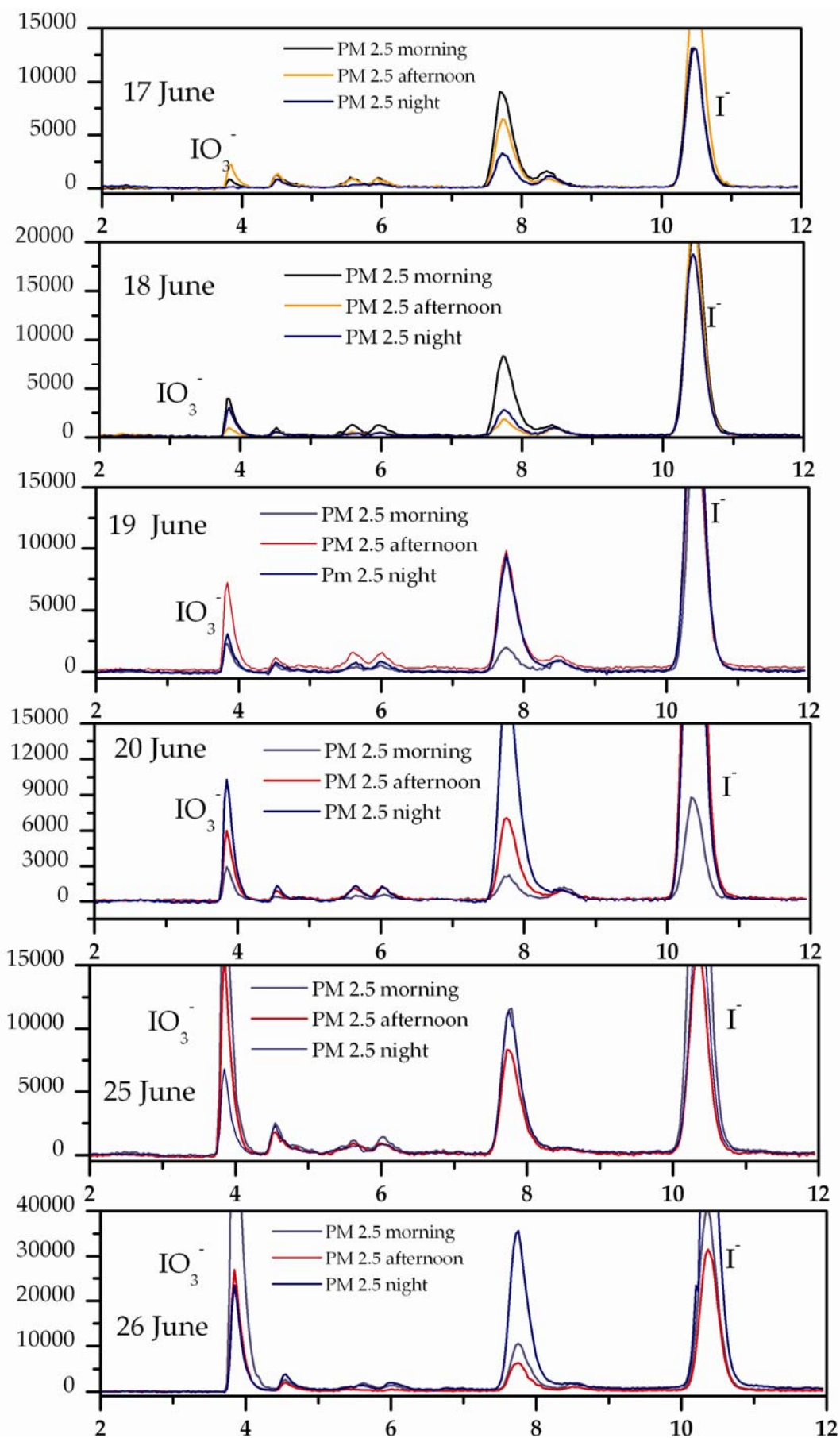
NOAA HYSPLIT MODEL
Backward trajectories ending at 08 UTC 05 Jul 06
FNL Meteorological Data



Sup. Fig. 9: Back trajectories for samples taken on the 4th July.



Sup. Fig. 10: IC-ICP-MS chromatograms of aerosol samples from Mace Head and offshore aboard the Celtic explorer.



Sup. Fig. 11: PM 2.5 chromatograms of aerosols from Mace Head.

References

- Baker, A.R.: Inorganic iodine speciation in tropical Atlantic aerosol, *Geophysical Research Letters*, 31, L23S02, 2004. DOI: 10.1029/2004GL020144
- Baker, A.R.: Marine aerosol iodine chemistry: the importance of soluble organic iodine, *Environmental Chemistry*, 2, 295-298, 2005.
- Baker, A.R., Thompson, D., Campos, A.M., Parry, S.J. and Jickells, T.D.: Iodine concentrations and availability in atmospheric aerosol, *Atmospheric Environment*, 34, 4331-4336, 2000.
- Baker, A.R., Tunnicliffe, C. and Jickells, T.D.: Iodine speciation and deposition fluxes from the marine atmosphere, *Journal of Geophysical Research*, 106, 28743-28749, 2001.
- Biester, H., Keppler, F., Putschew, A., Martinez-Cortizas, A. and Petri, M.: Halogen Retention, Organohalogenes and the Role of Organic Matter Decomposition on Halogen Enrichment in Two Chilean Peat bogs, *Environmental Science and Technology*, 38, 1984 - 1991, 2004.
- Bigg, E.K.: Source, nature and influence on climate of marine airborne particles, *Environmental Chemistry*, 4, 155-161, 2007.
- Caine, J.M.: Understanding the origin of clouds, *Environmental Chemistry*, 4, 141-142, 2007.
- Caine, J.M., Keywood, M., Bigg, E.K., Grose, M.R., Gillett, R.W. and Meyer, M.: Flux chamber study of particle formation from *Durvillaea potatorum*, *Environmental Chemistry*, 4, 151-154, 2007.
- Campos, M.L.A.M., Nightingale, P.D. and Jickells, T.D.: A comparison of methyl iodide emissions from seawater and wet depositional fluxes of iodine over the southern North Sea, *Tellus*, 48B, 106-114, 1996.
- Chin, W.-C., Orellana, M.V. and Verdugo, P.: Spontaneous assembly of marine dissolved organic matter into polymer gels, *Nature*, 391, 568-572, 1998.
- de Benoist, B., Andersson, A., Egli, I., Takkouche, B. and Allen, H., Iodine status worldwide. World Health Organization, Geneva (2004), pp. 1-46.
- Duce, R.A., Winchester, J.W. and Van Nahl, T.W.: Iodine, bromine, and chlorine in the Hawaiian marine atmosphere, *Journal of Geophysical Research*, 70, 1775-1799, 1965.
- Enami, S., Vecitis, C.D., Cheng, J., Hoffmann, M.R. and Colussi, A.J.: Global inorganic source of atmospheric bromine, *The journal of physical chemistry A: letters*, ASAP article, DOI: 10.1021/jp074903r S071089-075639(074907)004903-074901, 2007.
- Fuge, R. and Johnson, C.C.: The geochemistry of iodine - a review, *Environmental Geochemistry and Health*, 8, 31-54, 1986.
- Gilfedder, B.S., Petri, M. and Biester, H.: Iodine and bromine speciation in snow and the effect of orographically induced precipitation, *Atmospheric Chemistry and Physics*, 7, 2661-2669, 2007a.
- Gilfedder, B.S., Petri, M. and Biester, H.: Iodine speciation in rain and snow: Implications for the atmospheric iodine sink, *Journal of Geophysical Research*, 112, doi:10.1029/2006JD007356, 2007b.
- Keppler, F., Eiden, R., Niedan, V., Pracht, J. and Schöler, H.F.: Halocarbons produced by natural oxidation processes during degradation of organic matter, *Nature*, 403, 298-301, doi:10.1038/35002055, 2000.
- Krupp, G. and Aumann, D.C.: The origin of iodine in soil: I. Iodine in rainfall over Germany, *Chemie der Erde*, 59, 57-67, 1999.

- Leck, C. and Bigg, E.K.: Source and evolution of marine aerosol-A new perspective, *Geophysical Research Letters*, 32, L19803, DOI: 19810.11029/12005GL023651, 2005.
- Leck, C. and Bigg, E.K.: Comparison of sources and nature of the tropical aerosol with the summer high Arctic aerosol, *Tellus*, Online, DOI: 10.1111/j.1600-0889.2007.00315.x, 2007.
- Manley, S.L., Wang, N.-Y., Walser, M.L. and Cicerone, R.J.: Methyl halide emissions from greenhouse-grown mangroves, *Geophysical Research Letters*, 34, L01806, doi:10.1029/2006GL027777, 2007.
- McFiggans, G.: Marine aerosols and iodine emissions, *Nature*, 433, E13, 2005.
- McFiggans, G., Coe, H., Burgess, R., Allan, J., Cubison, M., Alfarra, M.R., Saunders, R., Saiz-Lopez, A., Plane, J.M.C., Wevill, D.J., Carpenter, L.J., Rickard, A.R. and Monks, P.S.: Direct evidence for coastal iodine particles from *Laminaria* macroalgae - Linkage to emissions of molecular iodine, *Atmospheric Chemistry and Physics*, 4, 701-713, 2004.
- McFiggans, G., Plane, J.M.C., Allan, B.J. and Carpenter, L.J.: A modeling study of iodine chemistry in the marine boundary layer, *Journal of Geophysical Research*, 105, 14371-14385, 2000.
- Moyers, J.L. and Duce, R.A.: Gaseous and particulate iodine in the marine atmosphere, *Journal of Geophysical Research*, 77, 5229-5238, 1972.
- O'Dowd, C.D., Facchini, M.C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y.J. and Putaud, J.P.: Biogenically driven organic contribution to marine aerosol, *Nature*, 431, 676, 2004.
- O'Dowd, C.D. and Hoffmann, T.: Coastal new particle formation: a review of the current state-of-the-art, *Environmental Chemistry*, 2, 245-255, 2005.
- O'Dowd, C.D., Jimenez, J.L., Bahreini, R., Flagan, R.C., Seinfeld, J.H., Hameri, K., Pirjola, L., Kulmala, M., Jennings, S.G. and Hoffmann, T.: Marine aerosol formation from biogenic iodine emissions, *Nature*, 417, 632-636, 2002.
- Orellana, M.V. and Verdugo, P.: Ultraviolet radiation blocks the organic carbon exchange between the dissolved phase and the gel phase in the ocean, *Limnology and Oceanography*, 48, 1618-1623, 2003.
- Pechtl, S., Schmitz, G. and von Glasow, R.: Modeling iodide iodate speciation in atmospheric aerosol, *Atmospheric Chemistry and Physics Discussions*, 6, 10959-10989, 2006.
- Pechtl, S., Schmitz, G. and von Glasow, R.: Modelling iodide – iodate speciation in atmospheric aerosol: Contributions of inorganic and organic iodine chemistry, *Atmospheric Chemistry and Physics*, 7, 1381–1393, 2007.
- Rancher, J. and Kritz, M.A.: Diurnal fluctuations of Br and I in the tropical marine atmosphere, *Journal of Geophysical Research*, 85, 5581-5587, 1980.
- Rosinski, J. and Parungo, F.: Terpene-Iodine compounds as ice nuclei, *Journal of Applied Meteorology*, 5, 119–123, 1966.
- Saiz-Lopez, A. and Plane, J.M.C.: Novel iodine chemistry in the marine boundary layer, *Geophysical Research Letters*, 31, L04112; DOI: 10.1029/2003GL019215, 2004.
- Saiz-Lopez, A., Plane, J.M.C., McFiggans, G., Williams, P.I., Ball, S.M., Bitter, M., Jones, R.L., Hongwei, C. and Hoffmann, T.: Modelling molecular iodine emissions in a coastal marine environment: the link to new particle formation, *Atmospheric Chemistry and Physics*, 6, 883-895, 2006.
- Saunders, R.W. and Plane, J.M.C.: Formation pathways and composition of iodine oxide ultra-fine particles, *Environmental Chemistry*, 2, 299-303, 2005.
- Schlegel, M.L., Reiller, P., Mercier-Bion, F., Barre, N. and Moulin, V.: Molecular environment of iodine in naturally iodinated humic substances: Insights from X-ray absorption spectroscopy, *Geochimica et Cosmochimica Acta*, 70, 5536-5551, 2006.
- Schnell, D. and Aumann, D.C.: The origin of iodine in soil: Iodine in soils of Germany, *Chemie der Erde*, 59, 69-76, 1999.

- Sellegrì, K., Yoon, Y.J., Jennings, S.G., O'Dowd, C.D., Pirjola, L., Cautenet, S., Chen, H. and Hoffmann, T.: Quantification of coastal new ultra-fine particles formation from *in situ* and chamber measurements during the BIOFLUX campaign, *Environmental Chemistry*, 2, 260-270, 2005.
- Seto, F.Y.B. and Duce, R.A.: A laboratory study of iodine enrichment on atmospheric sea-salt particles produced by bubbles, *Journal of Geophysical Research*, 77, 5339-5349, 1972.
- Sive, B.C., Varner, R.K., Mao, H., Blake, D.R., Wingenter, O.W. and Talbot, R.: A large terrestrial source of methyl iodide, *Geophysical Research Letters*, 34, L17808; DOI: 10.1029/2007GL030528, 2007.
- Sturges, W.T. and Barrie, L.A.: Chlorine, bromine and iodine in arctic aerosols, *Atmospheric Environment*, 22, 1179-1194, 1988.
- Toyota, K., Kanaya, Y., Takahashi, M. and Akimoto, H.: A box model study on photochemical interactions between VOCs and reactive halogen species in the marine boundary layer, *Atmospheric Chemistry and Physics*, 4, 1961-1987, 2004.
- Truesdale, V.W. and Jones, S.D.: The variation of iodate and total iodine in some UK rainwater samples during 1980-1981, *Journal of Hydrology*, 179, 67-86, 1996.
- Väkevää, M., Hämeri, K. and Aalto, P.P.: Hygroscopic properties of nucleation mode and Aitken mode particles during nucleation bursts and in background air on the west coast of Ireland, *Journal of Geophysical Research*, 107, 8104, 2002.
- Vogt, R., Sander, R., von Glasow, R. and Crutzen, P.J.: Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study, *Journal of Atmospheric Chemistry*, 32, 375-395, 1999.
- Whalley, L.K., Furneaux, K.L., Gravestock, T., Atkinson, H.M., Bale, C.S.E., Ingham, T., Bloss, W.J. and Heard, D.E.: Detection of iodine monoxide radicals in the marine boundary layer using laser induced fluorescence spectroscopy, *Journal of Atmospheric Chemistry*, 58, 19-39, 2007.
- Wong, G.T.F. and Cheng, X.H.: The formation of iodide in inshore waters from the photochemical decomposition of dissolved organic iodine, *Marine Chemistry*, 74, 53-64, 2001.

Chapter 3:

Terrestrial systems

3.1 A thermo extraction-UV/Vis-photospectrometric method for total iodine quantification in soils and sediments

B. S. Gilfedder¹, F. Althoff, M. Petri² and H. Biester¹

1. *Institut für Umweltgeochemie, Neuenheimer Feld 236 69120 Heidelberg Germany*

2. *Bodensee-Wasserversorgung, Sipplingen Laboratory Germany*

Status: published *Analytical and Bioanalytical Chemistry*

Abstract

Iodine in soils and sediments is a difficult element to analyze due to its volatility in acidic conditions. Traditionally it has been quantified using neutron activation analysis techniques, which, unfortunately, requires access to a nuclear reactor. We present here a simple method for solid phase iodine analysis by thermo extraction at 1000 °C and quantification by UV/Vis-photometry. Samples are combusted in an oxygen stream and trapped in Milli-Q water. The extracts are then quantified by an As³⁺-Ce⁴⁺ spectrometric method whereby iodide catalyzes the oxidation of As³⁺ to As⁵⁺ and reduction of Ce⁴⁺ to Ce³⁺. Three standard reference materials were analysed with excellent recoveries (97-113 %) and RSDs (<5 %). Moreover, the detection limit was less than 50 ng absolute iodine with a confidence limit of 95 %. When applied to carbonate rich samples from sediment traps deployed in Lake Constance we found very low iodine levels (0.8-2 mgkg⁻¹). Despite the low concentrations, the precision of the method was consistently better than 5 % RSD. However, the method needed to be slightly modified for organic and iodine rich sediments (20-30 % org-C) from a lake in the Black Forest by increasing the oxygen flow rate and decreasing the combustion time. Using the modified method we were able to achieve RSDs lower than 5 %.

3.1.1 Introduction

Iodine is an essential trace element for all mammals including humans. Iodine deficiency disorders are currently thought to affect up to 30 % of the world's population, in both developed and less developed nations (de Benoist et al., 2004). For example, it is estimated that the prevalence of goiter in Europe has risen by ~ 80 % since 1993 and currently more than half of the European population has insufficient iodine intake despite the addition of iodine to salt (de Benoist et al., 2004). One factor influencing iodine deficiency in continental regions is the concentration of iodine in the soil, as this has a direct influence on the natural iodine levels available for human (and other animals) uptake via plant foodstuffs and dairy products. However, iodine is relatively difficult to analyse in the solid phase. In acid assisted digestions, such as the commonly used aqua-regia procedure for metal extraction, iodine is converted to volatile I₂ and is lost to the gas phase; a process exacerbated by heating. Neutron Activation Analysis (NAA; instrumental, chemical or photo, see Wagner et al. for an

example, (Wagner et al., 1998)) is the industry standard for iodine analysis in solids and has been applied for at least the last 30 years. However, it is not available to all groups as it requires access to a nuclear reactor and is expensive to commission when a large number of samples need to be analysed. Analysis by external laboratories also has the disadvantage that the sample-submitter does not have any control over the operating conditions (e.g. decay and counting time) and samples are usually run in conjunction with many other samples with various matrices and iodine concentrations. Also, detection limits quoted from commercial laboratories are no lower than 1 mg kg^{-1} , which can be a significant problem in low iodine content soils and rocks. Other procedures such as fluxing with KOH-KNO₃ (Brown et al., 2005) requires expensive quantification equipment such as an ICP-MS to achieve sufficiently low detection limits and are relatively time consuming when many samples need to be processed. Other, less commonly used techniques, such as derivatization after dry ashing and analysis by GC-MS (Marchetti et al., 1994) require a relatively large number of steps and so are also quite time consuming. Such analytical limitations are particularly important in less developed countries where significant proportions of the population suffer from iodine deficiency disorders while laboratories are often rather rudimentary. Here we present a thermo-extraction method followed by Vis-spectrometry for iodine quantification in solid materials. Most importantly, this procedure is cheap despite having detection limits below 50 ng at 95 % confidence and a RSD of 3-5 %.

3.1.2 Material and methods

3.1.2.1 Chemicals

Starting reagents: All water used was from a Milli-Q $18 \text{ M}\Omega \text{ cm}^{-1}$ system. The following chemical solutions are taken from German norm method DIN 38405-33 (DIN 38405-33, 2001). Firstly, a 11.12 mol L^{-1} sulfuric acid stock solution was made from 97 % H₂SO₄, and 4.5 mol L^{-1} HCl stock solution was made from 37 % HCl. A 16 mmol L^{-1} Ce(SO₄)₂·4H₂O solution was made by mixing 400 ml water with 35 ml of the stock H₂SO₄ solution, to which 3.20 g of pro analysis Ce(SO₄)₂·4H₂O was added and dissolved with a magnetic stirrer. The Ce(SO₄)₂·4H₂O solution was then made up to 500 ml with water and stored for future use. A 15 mmol L^{-1} As₂O₃ solution was made by first dissolving 2 g NaOH and 3.71 g pro analysis As₂O₃ in 200 ml warm water. Once the As was dissolved the solution was acidified by addition of 53 ml of the H₂SO₄ stock solution and made up to 500 ml. It was then stored for future use. Calibration standards were made from ICP-MS grade 1000 mg l^{-1} iodide stock solution and were diluted to 10-160 $\mu\text{g l}^{-1}$.

3.1.2.2 Thermal iodine extraction

The thermal iodine extraction procedure employed here is very similar to that of Schnetger and Muramatsu (Schnetger and Muramatsu, 1996) and Putschew et al. (Putschew et al., 2003). This study used a Thermo-AOX (ECS2000 Euroglass Analytical Instruments) with automatic sample injection. This apparatus is simply a quartz combustion tube passing through a furnace capable of 1000 °C (Schnetger and Muramatsu (Schnetger and Muramatsu, 1996) state that 800 °C is enough for iodine extraction). The combustion tube is then connected to a glass iodine trap filled with Milli-Q water (Figure 1).

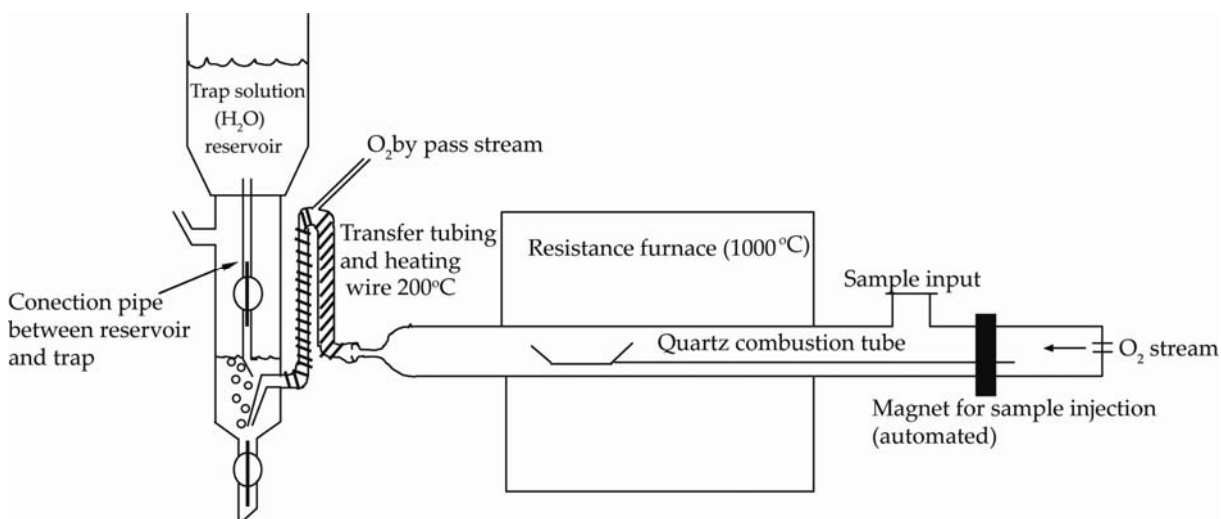


Figure 1: Set up of thermo-extraction apparatus. This is essentially the combustion and trapping parts of an AOX machine (Euroglass ECS2000). Not to scale.

Note that our method differs from that of Schnetger and Muramatsu (Schnetger and Muramatsu, 1996) and Putschew et al. (Putschew et al., 2003), in that we did not add a reducing agent (such as sulfite or sulfide) to the trapping solution. No loss of iodine was found due to sorption to the glass walls or volatilisation. The AOX machine was modified by removing the colorimetric cell used for standard AOX measurement, draining and thoroughly washing the sulfuric acid bubbler and using this bubbler as the iodine trap. The connecting glass pipe between the furnace and the trap was also heated to 200 °C with resistance heating wire. Each dried soil or sediment sample (7.8-300 mg) was weighed into a quartz ‘boat’ and placed in the quartz tube under an oxygen stream of 150 mlmin⁻¹ and a bypass oxygen flow rate of 40 mlmin⁻¹. The boat was then slowly (automatically) moved into the hot part of the furnace where-after the iodine vapor released on combustion was collected in the trap solution (Figure 2). The settings for the automated injection were: injection speed 2 mm/second, drying time 2 minutes, combustion time 5 minutes. After each sample had spent 5 minutes in the furnace the trap was drained into a test-tube and filled to the nearest volume marker. This

volume was then recorded for later quantification. Typically the trap contained 9-13 ml of water. An overview of the method is presented in Figure 2.

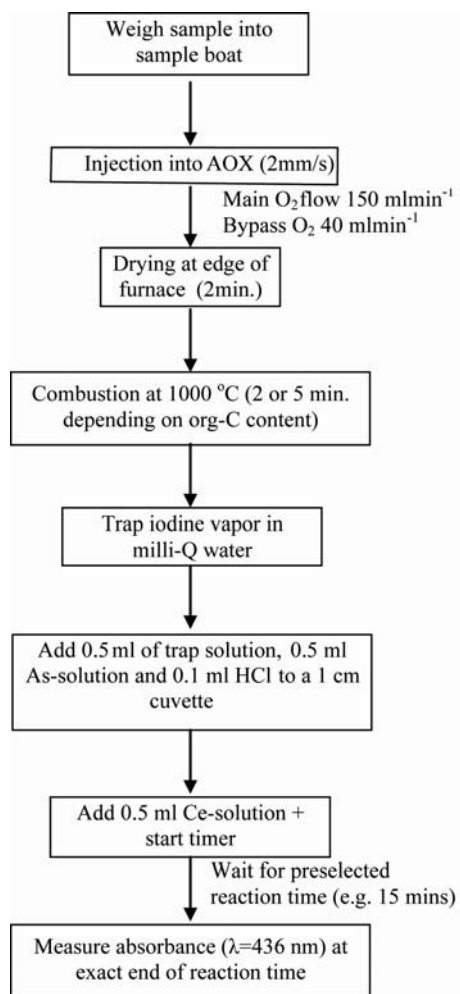


Figure 2: Flow chart of entire combustion and quantification procedures used for quantification of iodine in soils and sediments.

3.1.2.3 Quantification

The iodine quantification method used here is based on the German norm method DIN 38405-33 (DIN 38405-33, 2001) and is described in detail below. Iodide catalyzes the oxidation of aqueous As³⁺ to As⁵⁺ by Ce⁴⁺, which is reduced to Ce³⁺. In the absence of iodide the As-Ce redox reaction rate is so slow it is negligible for practical purposes, and as such the reaction rate can be quantitatively related to the iodide concentration in solution. Thus, the loss of the yellow coloured Ce⁴⁺ (measured as absorbance at λ=436 nm) after a preselected reaction time can be related directly to the aqueous iodide concentration. This reaction is relatively well studied and has been used for iodine quantification in seawater (Truesdale and Spencer, 1974; Elderfield and Truesdale, 1980), estuarine water (Ullman et al., 1988), sediment pore water (Ullman and Aller, 1980) and fresh water (Jones and Truesdale, 1984; Truesdale and Jones, 1996; Neal et al., 2007). Note that all other iodine species in solution,

such as iodate, are rapidly reduced to iodide by the excess concentrations of As^{3+} (Truesdale and Spencer, 1974). As the method is kinetically based (i.e. dependent on a reaction rate) the reaction is sensitive to temperature and, most importantly, the time allowed for the reaction to take place. Therefore the optical density (absorption) reading must always be taken after an exact pre-selected reaction time at constant (as possible) room temperature. In practice, perturbations in room temperature generally have only a minor effect on absorbance and can be easily corrected for by running a checking standard within each sample batch. The reaction time selected is the most important variable and needs to be selected depending on the estimated iodide concentration range in the sample solutions, as discussed later. The reaction rate is measured with a UV-Vis spectrometer at a wavelength of 436 nm at the preselected reaction time. The procedure followed was thus (and is summarised in Figure 2):

- 0.5 ml of sample (or calibration standard)
- 0.5 ml of the As^{3+} solution
- 0.1 ml of the HCl solution

Were added to a (disposable) 1 cm cuvette in this order, then

- 0.5 ml of the Ce^{4+} solution was added and at *exactly* the same time a timer was started
- The solution should be sucked up and ejected back into the cuvette 3 times to ensure adequate mixing.
- Record the absorbance at $\lambda = 436$ nm at *exactly* the end of the preselected reaction time. (e.g. after exactly 15 mins.)

The Ce^{4+} solution can be added to the next sample every 30 seconds or 1 minute depending on how familiar the user is with the method so that up to 30 samples can be run in a single 15-minute batch. Note that the same reaction time must be used for all samples and standards.

The sensitivity of this method is dependent on the reaction time selected, with higher sensitivities at longer reaction times. This is shown graphically in Figure 3 where the same standards are run at 5, 10 and 15 minutes reaction time. The optimum reaction time depends on the iodide concentration in the sample, and thus can be modified as the analyst requires, with lower iodide concentrations favoring a longer reaction time whereas higher iodide concentrations require a shorter reaction time. However, the working range of this photometric method is quite large, and in our experience from analysing standards, reference materials, and real samples 15 minutes reaction time is optimum for iodide concentrations between 10-100 $\mu\text{g l}^{-1}$. However, at iodide concentrations higher than 100 $\mu\text{g l}^{-1}$ the absorbance of Ce^{4+} is too low for reliable detection with the photometer. Therefore, 10 minutes reaction time is preferable for iodide concentrations greater than 100 $\mu\text{g l}^{-1}$. For concentrations between 1-10 $\mu\text{g l}^{-1}$ we have found that 35 minutes is an adequate reaction time using standards,

however, we did not find any soil extract concentrations in this range. Standard calibration solutions ($10\text{-}160\ \mu\text{g l}^{-1}$) of iodide were analysed prior to the reference materials and real samples using the above procedure and consistently gave r^2 values better than 0.9995. Note that the relationship between iodide concentration and optical density is inversely logarithmic. Therefore all absorbance data were transformed into a linear relationship by $A_{\text{new}} = \ln(1/A_{\text{sample}})$. If samples are to be run at a later time on the same day, a correction standard should also be run to account for any change in room temperature as mentioned above.

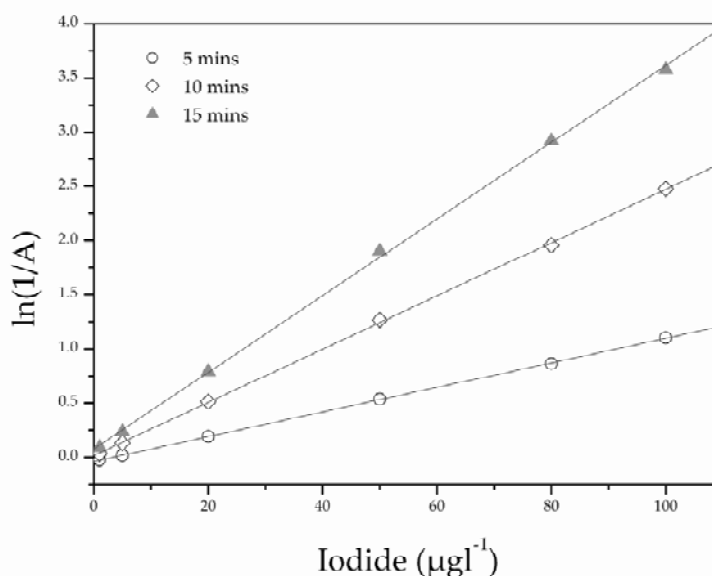


Figure 3: The effect of reaction time on transformed absorbance. Notice the increasing sensitivity with increasing reaction time.

3.1.2.4 Samples

Three standard reference materials with certified iodine concentrations were analysed to test the recovery, accuracy, precision, and reproducibility of the method:

1. Chinese stream sediment NCS DC 73312 with a certified iodine concentration of $2.9 \pm 0.4\ \text{mg kg}^{-1}$;
2. Chinese soil NCS DC 73321 with a certified iodine concentration of $9.4 \pm 1.1\ \text{mg kg}^{-1}$;
3. Montana soil SRM 2711 with a recommended iodine concentration of $3\ \text{mg kg}^{-1}$.

To test the precision of the method at low iodine concentrations, sediment samples were also obtained (from Langenargen Lake Research Center, Germany) from sediment traps deployed in Lake Constance, Germany. The carbonate dominated ($\sim 5\%$ inorganic-C), low organic carbon and low iodine content samples are presented here. We also sampled a 42 cm sediment core from the Mummelsee, a small humic-rich headwater lake (1036 masl) in the northern part of the Black Forest. Three selected samples from this core are presented to illustrate the applicability of the method to samples containing high organic carbon content (20-30 % org-C).

3.1.2.5 Detection limit

Calculating the detection limit for this method poses the problem that at lower iodine concentrations ever-larger masses of sample can be taken to ensure iodine levels are above instrument detection limits (Michel and Villemant, 2003). To overcome this problem we have calculated the minimum absolute (rather than mass per mass) iodine concentration that can be detected with 95 % confidence. For this calculation we have adopted the '95 % confidence interval' approach whereby known amounts of analyte are plotted vs. instrument response (in our case absorbance) and fitted with 95 % confidence limits. Calculation of the detection limit from the 95 % confidence intervals was performed according to German norm DIN 32645 (DIN 32645, 1994), which gives identical results to the statistical method suggested by (Clayton et al., 1987). This was accomplished by burning, trapping (in 12 ml water) and measuring (15 mins reaction time) increasing amounts (10-300 mg) of standard reference material NCS DC 73312 and plotting the transformed absorbance against absolute iodine mass (Figure 4). The detection limit given here must not be confused with the standard method of 3 times the standard deviation of the blank, which statistically only gives a detection certainty with 50 % confidence (Clayton et al., 1987; Sanders et al., 1996).

3.1.3 Results and Discussion

3.1.3.1 Reference materials

Iodine recoveries from the standard reference materials were consistently in the range given in the certificates and varied between 97-113 % for all samples (Table 1). The average value for the the Chinese stream sediment was $3.09 \pm 0.15 \text{ mgkg}^{-1}$ (n=15), whereas the average iodine concentration in the Chinese soil was $9.51 \pm 0.22 \text{ mgkg}^{-1}$ (n=18). Although no error is given for the Montana soil standard reference material, the recovery was also very good compared to the recommended value of 3 mgkg^{-1} (2.9 mgkg^{-1} , 97 %; Table 1). Moreover, the RSD for each run was usually less than 3.5 % for the Chinese reference materials. The RSD of all analysis, and so incorporating differences in daily calibrations etc., was $\sim 4.8 \%$ for the Chinese stream sediment and 2.3 % for the Chinese Soil. The weight of soil used did not appear to influence the result, as even using only 7.8 mg of the Chinese soil gave a recovery of 103 % (9.65 mgkg^{-1}) and 300 mg of the Chinese stream sediment gave 109 % (3.16 mgkg^{-1}), both well within the range given in the certificates (Table 1).

The plot of absolute iodine mass vs transformed absorbance used for quantification of the detection limit is shown in Figure 4. The regression coefficient was very good at $r^2 = 0.998$ despite the fact that it incorporates all potential errors in the method, from sample

heterogeneity, to weighing the sample into the boat and the combustion and photometric procedure. Based on the 95 % confidence intervals for this plot the detection limit was 49 ng iodine. For comparison with other studies that use the ‘3 times the standard deviation of the blank’ method we have also calculated the detection limit at 50 % confidence from confidence intervals to be 25 ng absolute iodine. However we do not recommend the use of this value as it is associated with a 50% chance of a type 2 error (i.e. a negative finding when in fact the analyte is present above the given detection limit) (Clayton et al., 1987; Sanders et al., 1996).

Table 1: Iodine recoveries from standard reference materials.

Sample name	Analysis Date	Ref. Value iodine (mgkg ⁻¹)	Weight (g)	Iodine found (mgkg ⁻¹)	Recovery (%)
Chinese Stream sediment NCS DC 73312	17/1/07	2.9 ± 0.4	0.1009	3.19	110 %
Chinese Stream sediment	17/1/07	2.9 ± 0.4	0.1194	3.28	113 %
Chinese Stream sediment	18/1/07	2.9 ± 0.4	0.1314	3.21	110 %
Chinese Stream sediment	25/1/07	2.9 ± 0.4	0.0572	2.85	98 %
Chinese Stream sediment	25/1/07	2.9 ± 0.4	0.0924	2.84	98 %
Chinese Stream sediment	25/1/07	2.9 ± 0.4	0.0509	2.94	102 %
Chinese Stream sediment	25/1/07	2.9 ± 0.4	0.1000	3.04	104 %
Chinese Stream sediment	30/1/07	2.9 ± 0.4	0.3006	3.16	109 %
Chinese Stream sediment	30/1/07	2.9 ± 0.4	0.0739	3.16	109 %
Chinese Stream sediment	06/2/07	2.9 ± 0.4	0.1142	2.96	102 %
Chinese Stream sediment	06/2/07	2.9 ± 0.4	0.1619	2.95	102 %
Chinese Stream sediment	06/2/07	2.9 ± 0.4	0.1017	3.09	106 %
Chinese Stream sediment	06/2/07	2.9 ± 0.4	0.0744	3.10	107 %
Chinese Stream sediment	09/2/07	2.9 ± 0.4	0.1148	3.13	108 %
Chinese Stream sediment	09/2/07	2.9 ± 0.4	0.0618	3.15	109 %
Chinese soil NCS DC 73321	17/1/07	9.4 ± 1.1	0.0985	9.58	102 %
Chinese soil	17/1/07	9.4 ± 1.1	0.0516	9.89	105 %
Chinese soil	17/1/07	9.4 ± 1.1	0.1110	9.63	102 %
Chinese soil	17/1/07	9.4 ± 1.1	0.0992	9.43	100 %
Chinese soil	17/1/07	9.4 ± 1.1	0.1474	9.60	102 %
Chinese soil	25/1/07	9.4 ± 1.1	0.0819	9.40	100 %
Chinese soil	25/1/07	9.4 ± 1.1	0.0599	9.84	105 %
Chinese soil	25/1/07	9.4 ± 1.1	0.0214	9.38	100 %
Chinese soil	25/1/07	9.4 ± 1.1	0.1002	9.85	105 %
Chinese soil	30/1/07	9.4 ± 1.1	0.0652	9.28	99 %
Chinese soil	30/1/07	9.4 ± 1.1	0.1025	9.23	98 %
Chinese soil	30/1/07	9.4 ± 1.1	0.0656	9.63	102 %
Chinese soil	30/1/07	9.4 ± 1.1	0.0484	9.51	101 %
Chinese soil	30/1/07	9.4 ± 1.1	0.0706	9.54	102 %
Chinese soil	06/2/07	9.4 ± 1.1	0.0561	9.17	98 %
Chinese soil	06/2/07	9.4 ± 1.1	0.0332	9.48	101 %
Chinese soil	06/2/07	9.4 ± 1.1	0.1086	9.21	98 %
Chinese soil	16/2/06	9.4 ± 1.1	0.0078	9.65	103 %
Montana soil SRM 2711	30/1/06	3 ± ?	0.0414	2.90	97 %

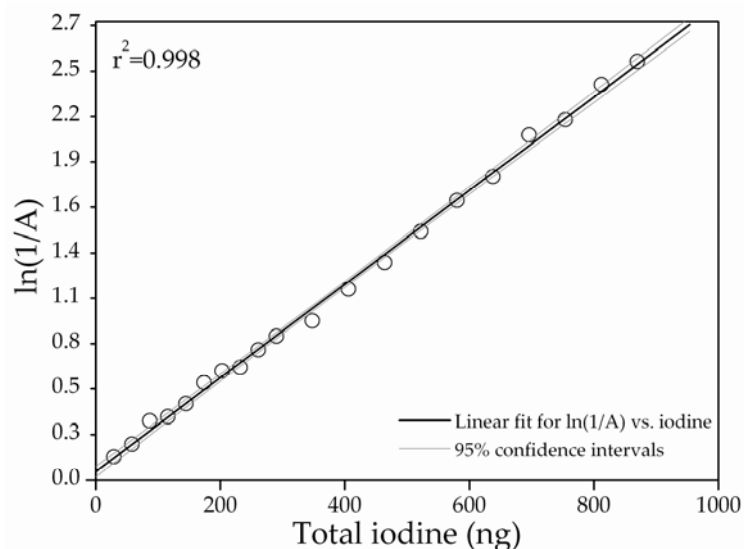


Figure 4: Absolute iodine concentrations from standard reference material NCS DC 73312 vs transformed absorbance $\ln(1/A)$. The confidence intervals for this graph were used to calculate the detection limit of 49 ng with 95 % certainty.

Real samples

As expected, the iodine concentrations in the carbonate rich sediment from the Lake Constance sediment traps were very low, ranging from 0.78-2.08 mgkg^{-1} for the two samples shown here (Table 2). Despite the low concentrations, the precision of the method was still very good, with a RSD of 1.3 % for the sediment trap sample containing 2.04 mgkg^{-1} and 4.8 % in the sample with an average of 0.82 mgkg^{-1} . These samples illustrate one of the advantages of this method; the weight of sample taken can be modified based on the expected iodine concentration in the sample. For example, when very low iodine concentrations are expected (e.g. $<2 \text{ mgkg}^{-1}$) more sample material can be burnt in the furnace to ensure that the absolute iodine concentration is above the 49 ng detection limit given above. This also applies to samples containing high iodine concentrations, i.e. a low weight of material can be selected to ensure that the iodine levels are not above the usual calibration curve. Indeed, high iodine levels in the extraction solution can be more of a problem than low concentrations, as, due to the inverse logarithmic nature of the calibration curve, higher sensitivity is observed at lower iodine concentrations. Moreover, when iodine levels are very high the Ce^{4+} is reduced too rapidly and all colour in the cuvette is lost. This can be circumvented by selecting a shorter reaction time to ensure that there is enough Ce^{4+} to give a reliable absorbance reading (Figure 3). Again this is true vice versa; a longer reaction time can be selected for low iodine concentrations.

When we applied the method described above to the organic rich Mummelsee sediments the RSDs were relatively high ($<10 \%$). Therefore we varied the oxygen flow rate, injection speed, evaporation time and combustion time in attempt to reduce the standard deviation to

less than 5 %. The most appropriate (i.e. lowest RSDs) method was with an increased oxygen flow rate ($\sim 225 \text{ mlmin}^{-1}$) and shorter burning period (2 minutes). The increased oxygen flow rate was necessary, as the organic carbon tended to combust at the edge of the furnace and the energy (heat) release during combustion probably volatilized a portion of the iodine. The higher oxygen flow ensured that any iodine volatilized at the edge of the furnace passed through the hot part of the furnace into the trapping solution. With this modified method iodine concentrations in the three core samples from the Mummelsee were significantly higher (8.5 ± 0.4 to $15 \pm 0.5 \text{ mgkg}^{-1}$) than those observed in the carbonate rich samples from Lake Constance with RSDs $< 5 \%$ (Table 2) The modified method also gave accurate results for the standard reference materials (Table 2).

Table 2: Iodine concentrations, standard deviations (mgkg^{-1}) and relative standard deviations (%) in sediments collected from sediment traps deployed in Lake Constance, (LC), and a sediment core from the Mummelsee (Ms), Black Forest, both from Germany. Iodine concentrations in standard reference materials using the modified method are also shown.

Sample	Sample date	Weight	Iodine mgkg^{-1}	Mean mgkg^{-1}	SD (mgkg^{-1})	RSD (%)
LC-5569	30/5 -14/6/05	0.1769	2.03	2.04	0.02	1.3
rep 1		0.1304	2.08			
rep 2		0.1861	2.04			
rep 3		0.1801	2.01			
rep 4		0.1645	2.05			
LC-5765	22-29/8/05	0.2443	0.84	0.82	0.04	4.8
rep 1		0.1423	0.89			
rep 2		0.1056	0.77			
rep 3		0.0989	0.79			
rep 4		0.1553	0.78			
rep 5		0.1599	0.81			
rep 6		0.1221	0.84			
Ms-4 cm	0.0338	12.14	12.48	0.58	4.6	
rep 1		0.0395				12.22
rep 2		0.0285				12.82
rep 3		0.0322				13.32
Ms-18 cm	0.0485	8.74	8.5	0.38	4.5	
rep 1		0.0540				7.96
rep 2		0.0354				8.49
Ms-28 cm	0.0313	15.04	15	0.5	3.3	
rep 1		0.0271				14.93
rep 2		0.0273				14.56
rep 3		0.0297				14.59
rep 4	0.0269	15.77				
NCS DC 73321		0.0649	9.68			
NCS DC 73312		0.0585	3.16			

3.1.4 Conclusions

We have presented here a relatively simple technique for iodine quantification in soils and sediments. When compared to standard reference materials the recoveries were between 97-

113 % depending on the reference material and were well within the error given in the certificates. All replicate analysis had RSD's below 5 % and the method had a detection limit of 49 ng absolute iodine with a 95 % confidence limit. Analysis of real sediment samples showed that organic rich sediments (> 15 % org-C) have significantly higher iodine concentrations than the carbonate rich and organic poor samples (inorg-C~5 %, org-C < 2 %). However, to obtain satisfactory results in the high org-C samples the method needed to be modified by increasing the oxygen flow rate and decreasing the combustion time.

The major benefit of this method is that the detection limit is significantly lower than commercially available NAA, which is not less than 1 mgkg⁻¹. Moreover, the method is less time consuming than dry fluxing at high temperatures with either ICP-MS or derivitisation combined with GC-MS quantification (Marchetti et al., 1994; Michel and Villemant, 2003). It also has low relative standard deviations comparable to, or lower than, other methods despite utilizing low cost technology. Indeed, the method is comparatively cheap and rapid compared to all other iodine quantification procedures, and, in particular, does not require access to a nuclear reactor as in NAA. As such, it is an ideally suited method for use in areas that are currently effected by iodine deficiency but do not have access to expensive analytical equipment.

3.1.5 Acknowledgements

We would like to thank Dr. M. Wessels from the Langenargen Lake Research Institute for the Lake Constance sediment trap samples. Two reviewers also contributed to improving the manuscript. This project was funded by the Deutsche Forschungsgemeinschaft to H. Biester under contract No. BI-734/4-5.

References

- Brown, C.F., Geiszler, K.N. and Vickerman, V.T.: Extraction and quantitative analysis of iodine in solid and solution matrixes, *Analytical Chemistry*, 77, 7062-7066, 2005.
- Clayton, C.A., Hines, J.W. and Elkins, P.D.: Detection limits with specified assurance probabilities, *Analytical Chemistry*, 59, 2506-2614, 1987.
- de Benoist, B., Andersson, A., Egli, I., Takkouche, B. and Allen, H., Iodine status worldwide. World Health Organization, Geneva (2004), pp. 1-46.
- DIN 32645, Chemische Analytik– Nachweis-, Erfassungs- und Bestimmungsgrenzen. Beuth, Berlin (1994).
- DIN 38405-33, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung - Anionen (Gruppe D) - Teil 33: Bestimmung von Iodid mittels Photometrie (D 33). Beuth, Berlin (2001), p. D33.

- Elderfield, H. and Truesdale, V.W.: On the biophilic nature of iodine in seawater, *Earth and Planetary Science Letters*, 50, 105-114, 1980.
- Jones, S.D. and Truesdale, V.W.: Dissolved iodine species in a British freshwater systems, *Limnology and Oceanography*, 29, 1016-1024, 1984.
- Marchetti, A.A., Rose, L. and Straume, T.: A simple and reliable method to extract and measure iodine in soils, *Analytica Chimica Acta*, 296, 243-247, 1994.
- Michel, A. and Villemant, B.: Determination of halogens (F, Cl, Br, I) sulfur and water in seventeen geological reference materials, *Geostandards Newsletter*, 27, 163-171, 2003.
- Neal, C., Neal, M., Wickham, H., Hill, L. and Harman, S.: Dissolved iodine in rainfall, cloud, stream and groundwater in the Plynlimon area of mid-Wales, *Hydrology and Earth System Sciences*, 11, 283-293, 2007.
- Putschew, A., Keppler, F. and Jekel, M.: Differentiation of the halogen content of peat samples using ion chromatography after combustion (TX/TOX-IC), *Analytical and Bioanalytical Chemistry*, 375, 781-785, 2003.
- Sanders, P.F., Lippincott, R.L. and Eaton, A.: Determining quantitation levels for regulatory purposes, *journal AWWA*, 88, 104-114, 1996.
- Schnetger, B. and Muramatsu, Y.: Determination of halogens, with special reference to iodine, in geological and biological samples using pyrohydrolysis for preparation and inductively coupled plasma mass spectrometry and ion chromatography, *Analyst*, 121, 1627-1631, 1996.
- Truesdale, V.W. and Jones, S.D.: The variation of iodate and total iodine in some UK rainwater samples during 1980-1981, *Journal of Hydrology*, 179, 67-86, 1996.
- Truesdale, V.W. and Spencer, C.P.: Studies on the determination of inorganic iodine in seawater, *Marine Chemistry*, 2, 33-47, 1974.
- Ullman, W.J. and Aller, R.C.: Dissolved iodine flux from estuarine sediments and implications for the enrichment of iodine at the sediment water interface, *Geochimica et Cosmochimica Acta*, 44, 1177-1184, 1980.
- Ullman, W.J., Luther, G.W., Aller, R.C. and Mackin, J.E.: Dissolved iodine behavior in estuaries along the east coast of the United States, *Marine Chemistry*, 25, 95-106, 1988.
- Wagner, K., Görner, W., Hedrich, M., Jost, P. and Segebade, C.: Analysis of chlorine and other halogens by activation with photons and neutrons, *Fresenius Journal of Analytical Chemistry*, 362, 382-386, 1998.

3.2 Iodine speciation and cycling in limnic systems: observations from a humic rich headwater lake (Mummelsee)

B. S. Gilfedder¹, M. Petri² and H. Biester¹

1. *Institut für Umweltgeochemie, Neuenheimer Feld 236 69120 Heidelberg, Germany*

2. *Bodensee-Wasserversorgung, Sipplingen Laboratory, Germany*

Status: Published online in *Biogeosciences Discussions*

Abstract

Iodine undergoes several redox changes in the natural environment, existing as iodate, iodide, and covalently bound to organic matter. While considerable attention has been given to iodine speciation and cycling in the marine environment, very little is known about iodine cycling and speciation in terrestrial fresh water systems. Here we show iodine speciation (measured by IC-ICP-MS) data from one year of monthly sampling of a small humic rich lake in the Black Forest (Mummelsee) under varying redox conditions. The aim was to elucidate the seasonal cycles of iodine species in the lake water column and to quantify both inorganic and organic iodine species. A sediment core was also collected for iodine analysis. Total iodine levels in the Mummelsee averaged $1.93 \pm 0.3 \mu\text{g l}^{-1}$. Organo-I was the dominant species in the lake, making up on average $85 \pm 7 \%$ of the total iodine. No strong seasonal variation in organo-I was observed, with only small variations occurring in the epi- and hypolimnion. Iodide was scavenged from the epilimnion during the summer and autumn, which could be related to (micro)biological uptake and co-precipitation. This was also suggested by the high iodine levels in the sediment core (av. $11.8 \pm 1.7 \text{ mg kg}^{-1}$). In the hypolimnion, a strong flux of iodide was observed from the sediments into the water column during anoxic and hypoxic conditions, observed during the summer, autumn and, in the bottom 2 m, the winter. This iodide flux was derived from the bottom sediments and is thought to occur during decomposition of biological material. Iodate levels in the epilimnion increased consistently over the year, whereas it was reduced below detection limits in the hypolimnion during low oxygen conditions. The winter partial turnover lead to reintroduction of oxygen into the hypolimnion and the formation of iodate and organo-I, as well as removal of iodide. In conclusions, iodine cycling in the Mummelsee was controlled by organo-I, although redox conditions were also important, particularly in the hypolimnion during stratification.

3.2.1 Introduction

Iodine species in fresh waters generally occur as iodide, iodate, and organically bound iodine. Under typical oxidizing conditions the inorganic iodine speciation should be dominated by iodate whereas iodide should be well below detection limits (Luther et al., 1995). The disequilibrium observed in both freshwater and oceanic environments, where significant concentrations of iodide ($0.3\text{-}20 \mu\text{g l}^{-1}$) have consistently been observed over at least the past four decades, has largely been attributed to biological activity and perhaps also to photolytic processes (Elderfield and Truesdale, 1980; Jones and Truesdale, 1984; Jickells et al., 1988;

Luther and Cole, 1988; Tian and Nicolas, 1995; Spokes and Liss, 1996; Cook et al., 2000; Wong and Cheng, 2001; Chance et al., 2007). It is becoming increasingly apparent that organically bound iodine also makes up a significant fraction of the aqueous iodine pool, particularly in near-shore and estuarine waters as well as at the interface between oxic and anoxic waters (Ullman et al., 1990; Luther and Campbell, 1991; Stipanicev and Branica, 1996; Wong and Cheng, 1998; Cook et al., 2000). For example, Stipanicev and Branica, (1996) have found up to 30 % organically bound iodine in Rogoznica Lake, a coastal cast depression filled with sea water. However, all of these studies are from marine or marine influenced environments and few analogous studies exist from freshwater systems. Moreover, while reports of total iodine concentrations in fresh waters are relatively numerous (e.g. Fuge and Johnson, 1986; Bird et al., 1995a; Oktay et al., 2001; Moran et al., 2002; Neal et al., 2007), detailed studies focusing on speciation are few and often one-off, intended only to develop a method (Reifenhäuser and Heumann, 1990; Rädlinger and Heumann, 1997; Heumann et al., 1998; Grüter et al., 2000; Wuilloud et al., 2003). Some of these studies have been vital in classifying the presence (e.g. Heumann et al., 1998 and references therein), and nature (Moulin et al., 2001; Reiller et al., 2006; Schlegel et al., 2006), of organically bound iodine, but are unable to elucidate any temporal trends or behaviour of iodine in the natural environment. Indeed, to the best of our knowledge there has only been one long-term systematic study on iodine speciation in freshwater, and in limnic systems in particular (Jones and Truesdale, 1984). This study was able to clarify inorganic iodine speciation cycles in two lakes with differing redox conditions and has not been superseded in detail or comprehensiveness despite 22 years of analytical advancements. It demonstrated that iodine is sensitive to water column redox changes and in the oxidized zone of the lake, iodide and iodate were not in equilibrium. In the anoxic hypolimnion iodide and chloroform extractable iodine were the only detectable iodine species. Unfortunately, due to the analytical capabilities of the time it was not possible to unequivocally quantify organically bound iodine. In relation to iodine speciation in anoxic environments it is also possible to draw from oceanic and estuarine analogs, where iodide is the dominant inorganic species in anoxic bottom waters and sediments (Wong and Brewer, 1977; Luther and Cole, 1988; Ullman et al., 1990; Luther and Campbell, 1991; Luther et al., 1995). For example, in the Cariaco Trench off the coast of Venezuela Wong and Brewer, (1977) observed direct conversion of iodate to iodide in a near 1:1 ratio at the oxic-anoxic boundary and also highlighted the release of iodide from sediments in the Black Sea. Similarly, Žic and Branica, (2006) have found reduction of iodate and release of iodide from sediments and during diagenesis of biological material in anoxic and hypoxic waters of a saline lake that has limited connection with the Adriatic Sea. However, the common theme throughout all of these studies has been the

inorganic aqueous iodine cycle. Perhaps due to problems with methodology it has been relatively difficult, up until recently, to accurately quantify the organically bound iodine fraction. However, with the wide spread use of ICP-MS it is now possible to unequivocally quantify total iodine without the need for lengthy chemical treatment (i.e. dehydrohalogenation; Schwehr and Santschi, (2003)). Furthermore, by coupling an ion-chromatograph to the ICP-MS, it is also possible to quantify iodide and iodate directly into the ng l^{-1} range. For example, organically bound iodine is the dominant species in peat bogs, although this is hardly unexpected given that concentrations of dissolved organic carbon often exceed 50 mg l^{-1} and even chlorine is bound to organic moieties (Biester et al., 2004). We present here a 12-month study of iodine speciation and cycling from a humic rich lake in the Black Forest, Germany, under changing redox conditions. The aim is to extend the earlier studies by Jones and Truesdale, (1984) on iodine cycling and speciation in freshwater lakes by analysing organic and inorganic iodine species as well as taking a sediment core for comparison with aqueous phase iodine levels.

3.2.2 Study site and Methods

The Mummelsee is a small humic ($\text{DOC} \sim 7 \text{ mg l}^{-1}$) cirque lake located in the northern part of the Black Forest, Germany, at 1036 masl (Figure 1). The lake has a maximum depth of 17 m, surface area of 3.7 ha and volume of $277\,500 \text{ m}^3$. It has only one very small spring inflow located two meters from the lake shore which means that, despite its small size, the lake has a water residence time of about 470 days (Thies, 1991). The lake has a catchment area of 18 ha, which is mostly forested by Norway spruce. Historically, as in many parts of the Black Forest, the Mummelsee and its catchment were affected by acid deposition, with the pH of the inflow and lake dropping to 4.4 and 5 respectively (Thies, 1987). Its susceptibility to acid conditions is mainly due to the underlying geology (early Triassic Red Sandstone; Buntsandstein) and acid podsol soils, both of which have a very low buffering capacity. Thies, (1987) speculated that during much of the French occupation of the catchment area after the second world war sewage was allowed to leak into the lake's catchment causing eutrophication. Also, heavy salting of the only road in the lake's catchment, which was previously used to access war and postwar (French occupation) radio and radar towers, caused relatively high Na, Cl and EC ($>100 \mu\text{s cm}^{-1}$) values. Our measurements have shown that the lake has, to a large degree, recovered since this time with EC dropping to $\sim 33 \mu\text{s cm}^{-1}$ and pH ranging from 6-7.

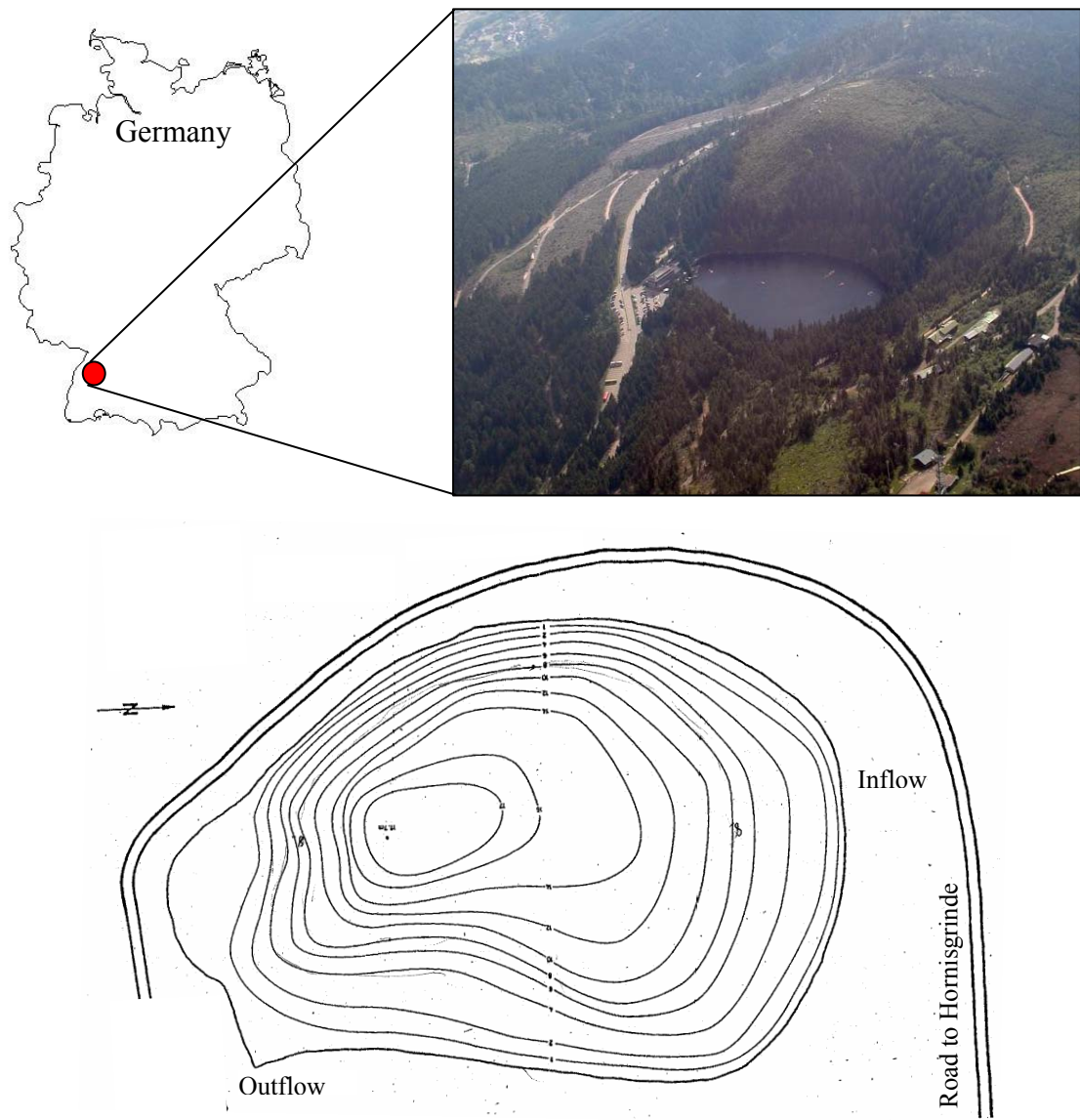


Figure 1: The Mummelsee study site. Maximum width of the lake is 180 m and max length is 280 m. Depth contours every 2 meters. The bathymetry map is oriented the same as the insert photo.

3.2.2.1 Water samples

The Mummelsee and its inflow were sampled monthly between April 2005 and May 2006. It was not possible to sample in December 2005 and March and April 2006 as the lake was covered with a thin layer of ice that could not be traversed but also did not allow a boat to pass over the lakes surface. When the lake was frozen in January and February 2006 samples were taken by drilling a hole through the snow and ice cover and lowering the UWITEC 1 L depth profile sampler into the waters below. Samples were taken every meter between the surface and 17 m depth. The temperature was recorded from the thermometer installed in the

sampler, EC, Eh, and after the first 4 months dissolved oxygen was also recorded in the field using standard electrode techniques. All samples for iodine and dissolved metals (Fe, Mn, Al, Si, Al) were filtered in the field (0.45 μm cellulose acetate) by syringe filtration directly after recording the temperature. Unfiltered samples were also collected for metal analysis to study the partitioning of metals between the operationally defined particulate ($>0.45 \mu\text{m}$) and dissolved ($<0.45 \mu\text{m}$) phases. This was done in an attempt to trace redox changes and any possible correlations between iodine species with (oxy)hydroxides. Samples for metal analysis were acidified in the field to $\text{pH}<2$ with 65 % suprapur (Merc) nitric acid and all samples were kept cool at 4°C until analysed. For iodine this was usually less than two weeks but always within one month, which should be adequate to preserve the original iodine speciation (Campos, 1997).

Total iodine concentrations were measured by inductively coupled plasma-mass spectrometry (ICP-MS) after adding ^{187}Re as an internal standard. Iodine species (iodide, iodate, and organically bound iodine) were analysed by coupling an ion chromatograph to the ICP-MS (IC-ICP-MS). Organically bound iodine was calculated as total iodine minus the sum of the inorganic species (i.e. $\text{Organo-I} = \text{total I} - (\text{I}^- + \text{IO}_3^-)$). Iodine species were quantified using a Dionex AS16 column with an AG16 guard column, 35 mmol NaOH eluent, a flow rate of 0.9 ml min^{-1} and a Meinhard nebulizer with a cyclone spray chamber on a Perkin Elmer Elan 6100 quadrupole ICP-MS. Samples were injected into the chromatographic system with a Perkin Elmer series 200 autosampler and the entire system was operated with Chromera software also from Perkin Elmer. This method has a detection limit for aqueous iodine species of about 30 ng l^{-1} and each sample has a run-time of only 12 minutes (Figure 2). Moreover, no sample pretreatment or chemical additives are required. Memory effects were evaluated by periodically running blank samples between regular samples, however all iodine species in blanks were consistently below detection limits. Replicates, triplicates or at most 7 replicates were analysed for selected samples in most sample batches and ranged from a relative standard deviation (RSD) of $<1\%$ to a maximum of 6%. Eight replicates for speciation were also run for a sample from the epilimnion over two days and are shown in Table 1. Iodate, at an average $0.15 \mu\text{g l}^{-1}$ concentration level, gave a standard deviation (STD) of $\pm 0.006 \mu\text{g l}^{-1}$ and a relative standard deviation (RSD) of 4 % whereas iodide, at a concentration level of $0.06 \mu\text{g l}^{-1}$ gave STD of $0.005 \mu\text{g l}^{-1}$ and a RSD of 8 %. The accuracy of total iodine and iodide concentrations were checked using standard reference material BCR-611. BCR-611 is a groundwater certified reference material for bromide that also gives indicative values for total iodine ($9.3 \pm 1.3 \mu\text{g l}^{-1}$), and iodide ($9.0 \pm 1.1 \mu\text{g l}^{-1}$). All of our values were consistently within the error given in the certificate and averaged $9.7 \mu\text{g l}^{-1}$ for total iodine and average 9.4

$\pm 0.4 \mu\text{g l}^{-1}$ for iodide. Metals were analysed using inductively coupled plasma - optical emissions spectrometry (ICP-OES) and checked with standard reference material NIST-1643e. All concentrations were within 10 % of the certificate value.

Table 1: Precision of iodine speciation by IC-ICP-MS. All concentrations in $\mu\text{g l}^{-1}$.

Replicate	Iodate	Iodide
Rep 1	0.16	0.06
Rep 2	0.15	0.06
Rep 3	0.15	0.06
Rep 4	0.15	0.06
Rep 5	0.15	0.07
Rep 6	0.16	0.05
Rep 7	0.15	0.06
Rep 8	0.14	0.07

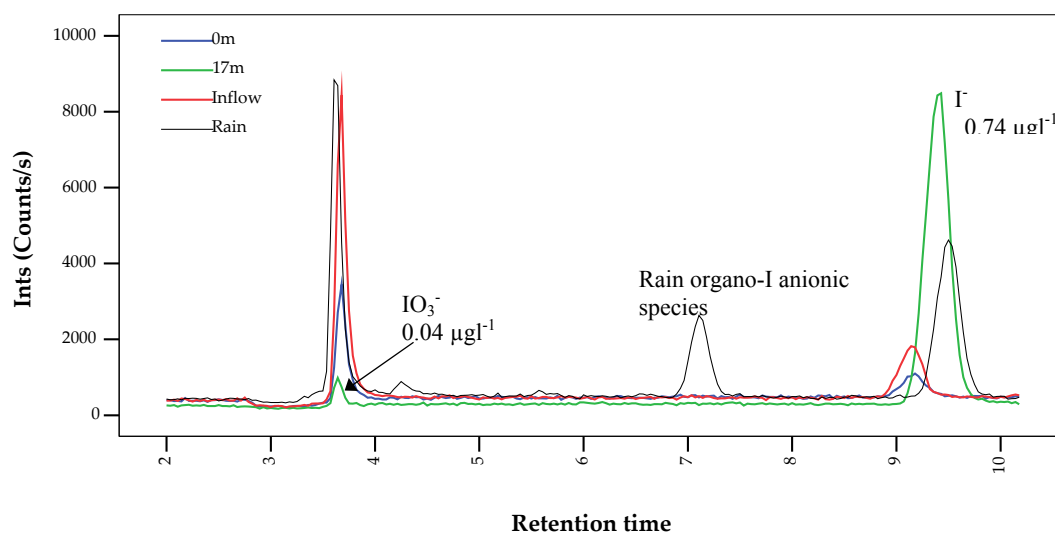


Figure 2: IC-ICP-MS iodine speciation chromatograms of samples from 0 m and 17 m depth, the spring inflow, and a rain sample collected on the shore of the lake. The rain sample is from the data in Gilfedder et al., (2007c).

3.2.2.2 Sediment core

A 42 cm sediment core was taken from the deepest part of the lake in October 2006 using a gravity corer and a 1 m Plexiglas tube. The core consisted of 42 cm black, organic rich sediment and 25 cm of the overlying water column. Only very minimal disturbance to the sediment/water interface occurred during sampling. The overlying water was highly anoxic at the time of sampling with a strong 'H₂S' smell. The core was taken directly to the cool room at Heidelberg University and after three days sectioned into 1 cm slices in a glove bag under

an N₂ atmosphere and transferred into 50 ml Falcon™ centrifuge tubes. The samples were then centrifuged (5000 rpm) and the supernatant, again in the glove bag, decanted into 15 ml test tubes. The porewater was subsequently analysed for total iodine by ICP-MS, however as they were unfiltered and probably were influenced by particle and humic material of high molecular weight it was decided not to report the results here. The porewater accounted for less than 0.5% of the total iodine. After pore water extraction the remaining sediment was freeze dried, milled in an agate ball mill and then analysed for total iodine concentrations as given in Gilfedder et al., (2007a). Briefly, each dried and milled sediment sample (20-50 mg) is placed in the quartz tube of an AOX machine and combusted in an oxygen stream at 1000°C. The released iodine vapour is then trapped in a connecting bubbler (formerly the sulfuric acid bubbler of the AOX) by Milli-Q water. Our system employed a Thermo-AOX (ECS2000 Euroglass Analytical Instruments) with automatic sample injection. The settings were: 2 mm s⁻¹ injection speed, 2 min drying time, and 2 min combustion time. The trapping solution was then analysed by an As-Ce spectrometric method whereby iodide quantitatively catalyses the reduction of Ce⁴⁺ by As³⁺ and loss of the yellow coloured Ce⁴⁺ is measured at 436 nm after a pre-selected reaction time in a UV/Vis spectrometer. Two standard reference materials, Chinese stream sediment (NCS DC 73312) and Chinese soil (NCS DC 73321), were analysed at the start, middle, and end of the sediment core to ensure the accuracy of the method. Also, each second sample was burned and analysed in triplicate to assess the precision of the method. This is given as 1 standard deviation of the mean in Figure 6 and was, in nearly all cases, less than 5 %. Two samples had a relative standard deviation of < 7 %. Total carbon was analysed with a LECO C/S analyzer. As this humic lake displays circum neutral pH values (6-7), and the sediments were a black/brown colour, total carbon was assumed to be solely composed of organic carbon, and the term ‘organic carbon’ is used throughout this manuscript. The first 21 cm of the core was dated by ²¹⁰Pb using the constant rate of supply model. The ²¹⁴Am bomb peak at 9 cm was taken as 1963 and then dating was extrapolated to the present day and back to the 21 cm 1841 ± 9.5 years. The ²¹⁴Am peak also agreed perfectly with the first ¹³⁷Cs peak, also at 9 cm depth. When extrapolating to the current day the 1-2 cm sample corresponded to 2005 ± 0.3 years; i.e. when the core was taken.

3.2.3 Results

3.2.3.1 Temperature profiles and stratification

The temperature depth profiles from the Mummelsee displayed patterns typical for lakes in temperate environments (Figures 3 and 4). In 2005, homothermy and spring overturn occurred

shortly before April and, as the spring and summer progressed, the lake became strongly stratified with the maximum depth of the epi- and metalimnion extending to 9 m. Late autumn and winter cooling of surface water caused a second, partial overturn and inverse stratification, with mixing occurring to ~15 m depth. As such the Mummelsee can be classified as a dimictic lake. As mentioned above, it appears that in autumn 2005 and spring 2006 the mixing was incomplete, with the bottom two meters of the lake remaining highly anoxic with $p_e \sim 0$ and a strong 'H₂S' smell. This is commensurate with depth profiles for redox sensitive elements Fe and Mn, which dramatically increase in concentration from Fe <100 $\mu\text{g l}^{-1}$ and Mn <10 $\mu\text{g l}^{-1}$ in the epilimnion to Fe >2 mg l^{-1} and Mn >80 $\mu\text{g l}^{-1}$ in the anoxic zone. The partial turnover was probably due to the Mummelsee being relatively sheltered from the wind by the bowl of the cirque.

3.2.3.2 Iodine speciation: Spring-Summer-Autumn

Thermal stratification and oxygen depletion in the hypolimnion during summer and autumn had a large influence on iodine concentrations and speciation in the Mummelsee (Figures 3 and 4). Initially, after the spring overturn, 2005, total iodine as well as all iodine species were relatively uniformly distributed throughout the profile, as expected for homothermy. Total iodine averaged $1.88 \pm 0.06 \mu\text{g l}^{-1}$ and iodide and iodate were approximately equal in concentration ($\sim 0.1 \mu\text{g l}^{-1}$). Organically bound iodine (organo-I) was by far the most abundant iodine species averaging $1.68 \mu\text{g l}^{-1}$, which is about 90 % of the total iodine (Figure 3). Organically bound iodine levels were relatively uniform over the spring-summer period (av. $1.6 \pm 0.15 \mu\text{g l}^{-1}$; 85 ± 7 % of total iodine) apart from a slight depletion with depth in the epilimnion during spring and an increase in this same area during the summer (Figure 3). There was also a decline in hypolimnic organo-I during September and October; however this trend was not continued into November. Organically bound iodine was consistently the dominant iodine species in the lake accounting for 70-95% of the total iodine. The lower percentages were from the hypolimnion where increasing iodide concentrations during stratification diluted the organically bound fraction.

During the spring to summer transition period iodate concentrations began to increase in the epilimnion; a trend that continued through the summer (maximum iodate concentration of $0.18 \mu\text{g l}^{-1}$) until the autumn-winter overturn. This iodate-enriched zone extended to a maximum depth of 8 m, observed in the November depth profile. In contrast, iodide, after an initial rise in June, began to decrease in concentration in the lake's epilimnion. This continued during the summer and autumn until iodide concentrations in the epilimnion were, by August, below the detection limit. The iodide decrease in the epilimnion was paralleled by a profound

increase in iodide in the hypolimnion. Concentrations in the hypolimnion increased from $\sim 0.15 \mu\text{g l}^{-1}$ after the spring turnover 2005 to $0.8 \mu\text{g l}^{-1}$ in late summer and autumn, an increase of more than 5 times. Moreover, iodide concentrations decreased consistently with height above the lake bottom, with a very distinct boundary between the epi- and hypolimnion. In contrast, iodate levels decreased in the hypolimnion during summer and autumn, with the change also occurring at the epi- hypolimnion boundary. The chemical distinction (i.e. redox boundary inferred from I^-/IO_3^- ratio, $\text{Mn}_{\text{part}}/\text{Mn}_{\text{dis}}$ and Fe) between the epilimnion and the hypolimnion became increasingly pronounced as the year progressed. However, the increase in iodide cannot be solely related to iodate reduction, as at most this could account for $<0.1 \mu\text{g l}^{-1}$ of the iodide. The increase in iodide concentrations in the hypolimnion was also matched by an increase in Fe, Mn, Si and in the Autumn, Al, and a decrease in dissolved oxygen (Figure 3). The epi- hypolimnion boundary for all these elements became increasingly defined as the year progressed. The large rise in Fe in the hypolimnion was mostly in the particle phase (i.e. $>0.45 \mu\text{m}$), whereas Mn showed no difference between particulate and dissolved concentrations. In contrast, in the oxic epilimnion Mn was dominantly in the particulate phase, with a sharp decline in dissolved Mn and an abrupt and commensurate increase in particulate Mn at the top of the hypolimnion.

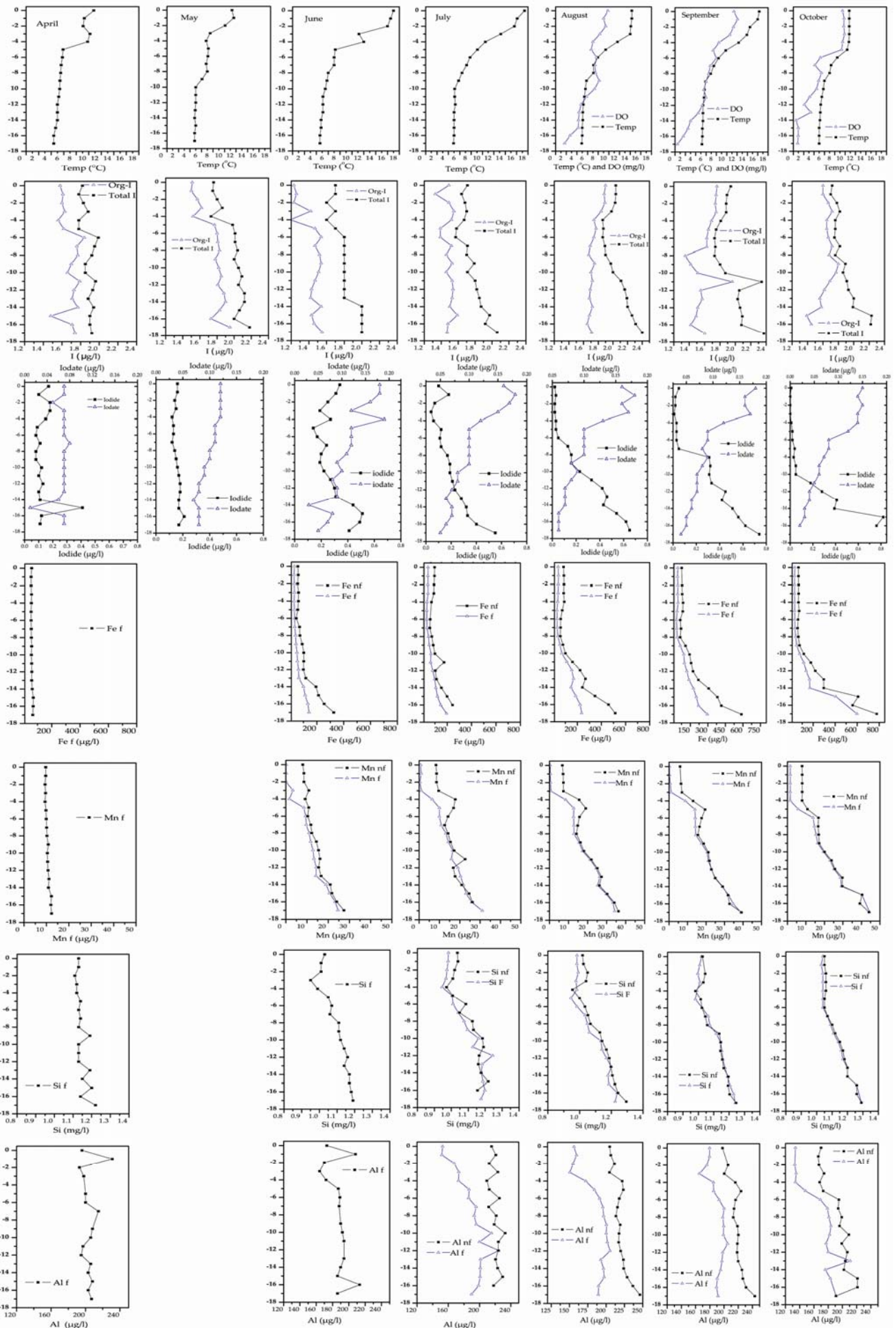


Figure 3: Depth profiles for the Mummelsee. April 2005 to October 2005. f=filtered, nf=not filtered.

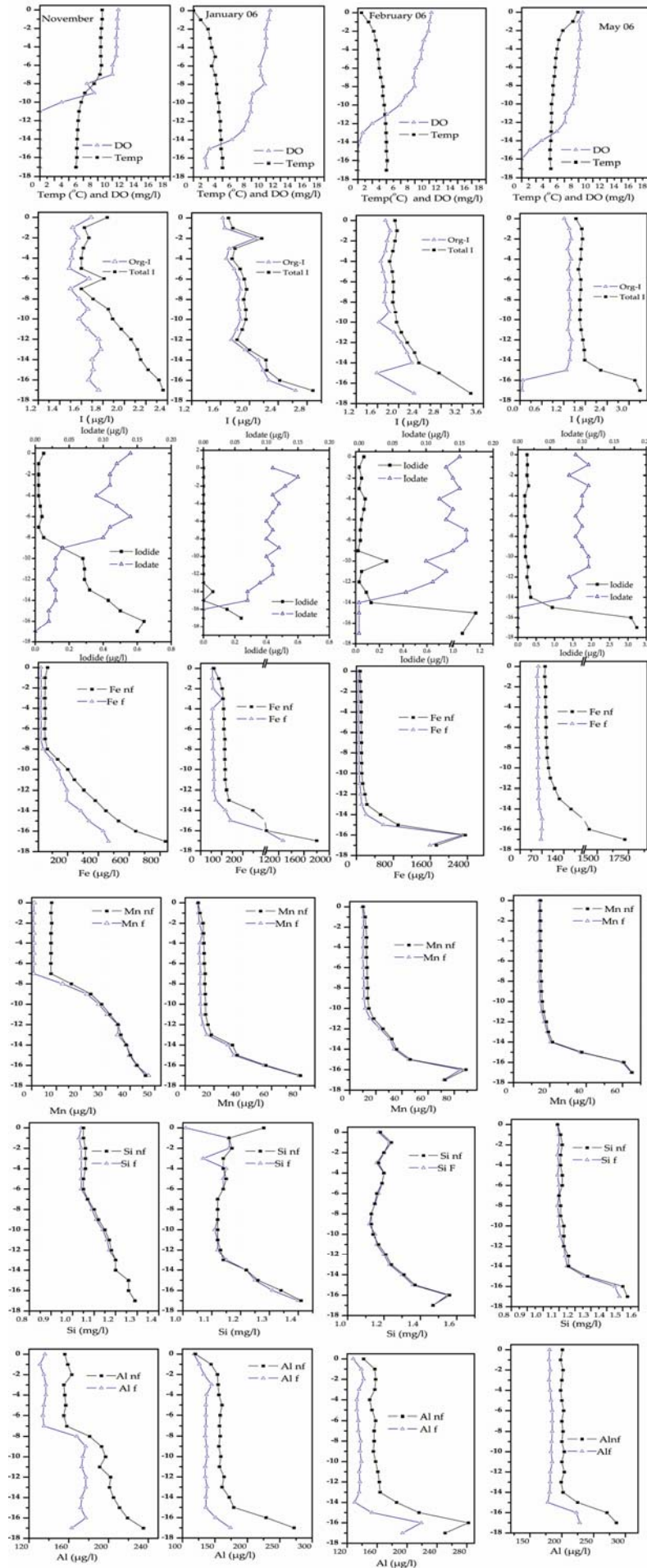


Figure 4: Depth profiles for the Mummelsee. November 2005 to May 2006. f=filtered, nf=not filtered.

3.2.3.3 Iodine speciation: winter and spring-2006

The top 15 m of the lake were well mixed during the winter turnover event, while the bottom 2 m remained anoxic and reducing (Figure 4). In the well-mixed layer, iodate ($0.14 \mu\text{l}^{-1}$) and organo-I ($\sim 1.7 \mu\text{l}^{-1}$) dominated the iodine speciation, whereas iodide was generally below the detection limit. Indeed, during this period organo-I very closely followed the total iodine concentrations, accounting for, on average, $94 \pm 3 \%$ of the total iodine. Metal concentrations were also relatively uniform in the well-mixed layer and showed little difference between particulate (as an indicator for oxidized (oxy)hydroxide species) and dissolved phases (reduced species); however levels of all elements began to rise at about 13 m depth, which also coincided with the largest decrease in oxygen levels. In contrast, iodate was absent from the anoxic bottom waters and iodide concentrations increased to a maximum of $1.2 \mu\text{g l}^{-1}$. The highly reducing nature of this zone is also shown by little difference between particulate and dissolved Fe (2 mg l^{-1}) and Mn ($100 \mu\text{g l}^{-1}$) levels. Qualitatively, we also noticed a strong 'H₂S' smell. It must be noted however, that in the February profile we did not take the first 16 samples from the deepest part of the lake and that after 16 m the sampler hit the lake bottom, making it necessary to bore another hole in the ice for the final 17 m sample. As such, the decrease in metal concentrations (and also a higher pe) in the final sample from February profile can be related to less reducing conditions at the new location. However, it can be clearly seen that this anoxic bottom layer influenced the chemistry of the overlying water column, consuming oxygen and iodate (particularly in February), and allowing iodide and metals to diffuse into the overlying water. A similar pattern was also observed after the spring 2006 turnover (May 2006), with the bottom 2 m remaining highly anoxic and rich in iodide ($3.24 \mu\text{g l}^{-1}$) and dissolved metals (except for Fe, which was mostly in the particulate phase), whereas the overlying water contained higher levels of dissolved oxygen and iodate and low levels of iodide and dissolved metals. Surprisingly, and in contrast to all other depth profiles, the anoxic zone in May 2006 also contained nearly no organically bound iodine, accounting for only 2-3 % of the total.

3.2.3.4 Inflow

The Mummelsee has only one small inflow; a spring located 2 m from the lake's northeastern side. This spring is derived from shallow groundwater, as the catchment is small and the Mummelsee is a headwater lake; located just below the summit of the highest mountain in the northern Black Forest (Hornisgrinde). The spring water was consistently oxygen saturated, as it cascaded over a small waterfall before entering the lake. Total iodine concentrations averaged $1.6 \pm 0.28 \mu\text{g l}^{-1}$ and apart from one high concentration in spring 2005, levels were

relatively uniform throughout the year (Figure 5). As observed in the lake, organically bound iodine was the dominant iodine species in the inflow, accounting for, on average, 76 % of the total iodine. Interestingly, iodate was considerably more abundant than iodide in all of the samples (molar IO_3^-/I^- range from 2.75-6.7; Figure 5), except for one sample from late autumn 2005 (molar IO_3^-/I^- 0.6) where concentrations were about equal. Iodide concentrations also appeared to increase during the summer to the late autumn maximum.

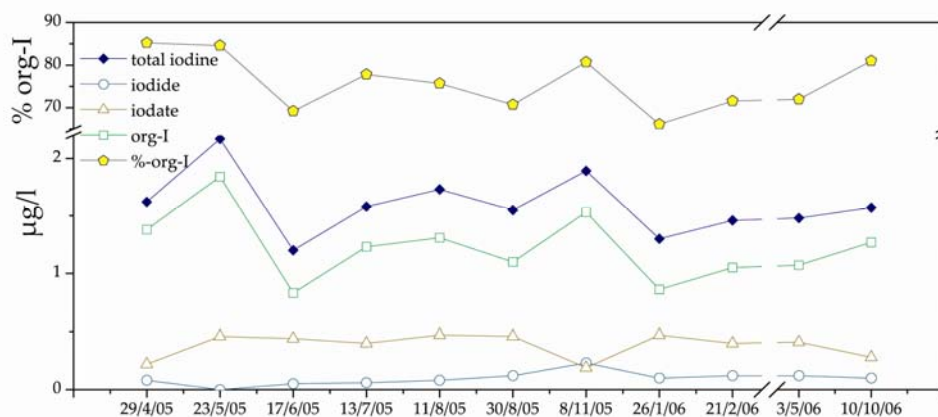


Figure 5: Total iodine concentrations and speciation in the spring inflow.

3.2.3.5 Sediment core

The first 21 cm of the 42 cm Mummelsee sediment core dated at 2005 to 1867. If we assume that the rate of sediment supply to each cm was constant, this gives a sedimentation rates ranging from 0.04 cm yr^{-1} at the lowest depth to 0.2 cm yr^{-1} at 14 cm depth. On average the sedimentation rate was 0.14 cm yr^{-1} . The core contained very high concentrations of organic material, ranging from 20-30 % org-C. Total iodine concentrations were also high, averaging $11.8 \pm 1.7 \text{ mg kg}^{-1}$, but were quite variable with depth and closely followed the organic-C curve (Figure 6). Regression analysis can be used as a more quantitative treatment of the relationship between organic-C and iodine. When the entire data set is used (treating organic C as the independent variable), there is only a weak ($r^2=0.28$), although statistically significant ($p<0.001$), relationship. However, on a closer inspection of the iodine-carbon profile it can be seen that it is, in fact, made up of two unique sections (Figure 7). Firstly, from 0-20 cm, where the iodine carbon ratio (defined as the gradient of the regression line with iodine in mg kg^{-1} and carbon in %) is 0.43, standard error = 0.1 and $r^2=0.52$ and then from 21-42 cm changes to 0.65, standard error 0.1 and $r^2=0.64$ (Figure 7). Both regressions are statistically significant ($p<0.001$). Interestingly, at the point where the I/C relationship appears to change there is a large spike, and then drop, in iodine concentrations.

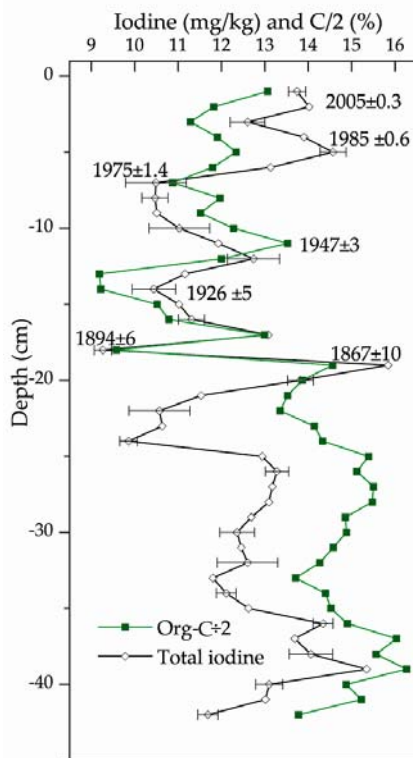


Figure 6: Total iodine and organic carbon in a 42 cm sediment core from the Mummelsee. Note that organic carbon concentrations are divided by 2 to allow better comparison. Error bars on total iodine represent 1σ of triplicate analysis.

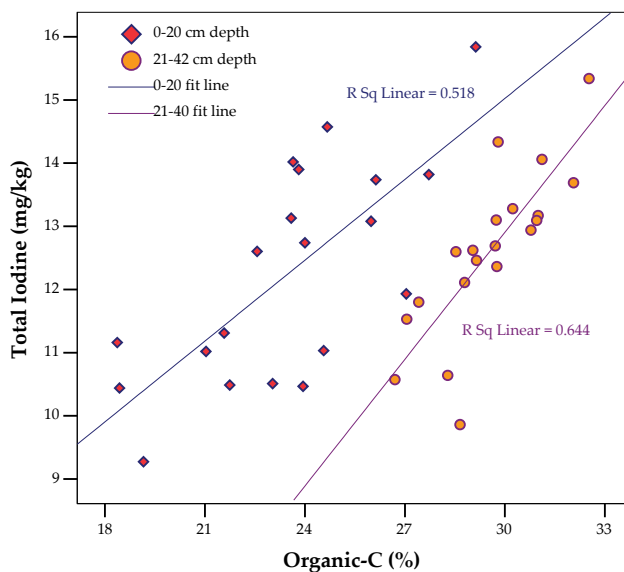


Figure 7: Total iodine vs. organic-C concentrations in sediments from 0-20 cm and 21-42 cm depth.

Some notable changes in the iodine sediment profile are spikes in concentrations in the top 6 cm (2005-1980), between 19-20 cm (1867-1884) and between 35-40 cm depth. Despite the variation in each sediment sample, which is related partially to sample heterogeneity and partially to the method, these spikes in iodine concentrations are significantly higher than general iodine concentrations. It is interesting to compare the sediment iodine concentrations to the overlying water column, from which most of the material is derived given the very low

stream inflow rate. It is immediately obvious that the iodine in the Mummelsee sediment is highly enriched relative to the overlying water column, with an enrichment factor, defined as the average iodine concentration in the sediment divided by the average iodine concentration in the epilimnion (taken as the top 7 m of the lake) and assuming 1 l water = 1 kg (so that we can dispense of the unit kg/l), of 6592.

3.2.4 Discussion

While most studies from freshwater environments focus on quantifying total iodine, speciation is a vital component in gaining a holistic view of the aqueous iodine cycle. In this section we first compare our iodine levels to other studies and then discuss iodine speciation and cycling in the Mummelsee.

The total iodine concentrations in the Mummelsee are similar to those reported for fresh water in other relatively remote headwater environments; although the different methods employed for quantifying total iodine must first be briefly discussed before a thorough comparison can be made. The most comprehensive study on iodine concentrations is undoubtedly from Neal et al., (2007), where 25 years of weekly to fortnightly iodine data from three tributaries located in Wales, UK, are compared. The average concentrations from the main streams were found to be 1-1.89 $\mu\text{g l}^{-1}$, which is very similar to our average value of 1.92 $\mu\text{g l}^{-1}$. However, Neal et al., (2007) used a spectrometric method based on the catalytic effect of iodide on the reduction of Ce^{4+} by As^{3+} . While this method is relatively inexpensive and has low detection limits, it has been shown by Wong and Cheng, (1998) that it only quantifies a portion of the organically bound iodine in addition to the inorganic species. As such, it may be misleading to compare ICP-MS data with Neal et al., (2007). This is highlighted by the fact that the Mummelsee, located in a relatively continental location at >1000 masl, has a higher average iodine concentrations than that observed in Wales, UK, a relatively maritime climate. Snyder and Fehn, (2004), in contrast, have analysed (ICP-MS) one-off surface water samples from every continent in the world, with a range from 0.125-137 $\mu\text{g l}^{-1}$ with higher concentrations generally occurring in arid environments. Our total iodine values lie within the lower range of their fresh water samples from Europe. Atarashi-Andoh et al.,(2007) have taken samples from various lakes in the English Lakes District and quantified total iodine with ICP-MS. The data ranged from 0.9-4.95 $\mu\text{g l}^{-1}$ over 8 lakes and appeared to depend on season with higher levels in autumn; a finding supported by the long-term measurements of Neal et al., (2007). From northern Germany, iodine levels taken from 'surface waters' are considerably higher than observed at our study site in the Black Forest, averaging 11.5 $\mu\text{g l}^{-1}$ (Szidat et al., 2000;

Michel et al., 2002). Rainwater collected from the Black Forest by Krupp and Aumann (1999), analysed by neutron activation analysis, were only slightly higher than the lake water concentrations found in the Mummelsee, averaging $2.2 \mu\text{g l}^{-1}$. Snow samples from the Mummelsee's surface taken during winter (Gilfedder et al., 2007b) had nearly identical concentrations ($1.84 \pm 0.17 \mu\text{g l}^{-1}$) to the lake and inflow water, strongly suggesting that the majority of iodine is derived from atmospheric deposition rather than from the lithosphere. Undoubtedly, many factors will influence the final concentrations of iodine in lakes and rivers, in particular, water-soil-rock interactions, evapoconcentration and a strong rainout effect that appears to be induced by increasing elevation (Fuge and Johnson, 1986; Oktay et al., 2001; Moran et al., 2002; Gilfedder et al., 2007b). Indeed, it is perhaps surprising that concentrations from the various areas in Europe are so similar over such wide geographical, geological and altitudinal regions. In contrast to these European sites, Moran et al., (2002) sampled a large number of rivers from the United States with an average value of $19.9 \mu\text{g l}^{-1}$ and median of $10.2 \mu\text{g l}^{-1}$. The majority of these samples were taken at the lower stretches of the rivers and, as such, integrate very large catchment areas that may include substantial anthropogenic iodine substances in addition to rock weathering and marine derived iodine. In particular, X-ray contrast media from hospitals are a known source of refractory anthropogenic iodine in aqueous environments. The two year study by Oktay et al., (2001), also from the USA, presents iodine concentrations from the Mississippi that are more in line with those observed in Europe, with an average (excluding unfiltered and replicate samples) of $5.55 \mu\text{g l}^{-1}$.

The iodine cycle in the Mummelsee can be broken into three components: 1) iodide release from the sediments during stratified anoxic conditions and scavenging from the epilimnion; 2) iodate increase in the epilimnion, production during the winter turnover, and reduction in the hypolimnion during stratification; and 3) the dominance of organically bound iodine in both the epi- and hypolimnion during all times of the year.

3.2.4.1 Iodide

Iodide concentrations in the epilimnion consistently declined throughout the summer and autumn period until iodide levels were below the detection limit. This suggests that iodide is preferentially removed from the surface waters. There are two possible processes for this removal, firstly, by (oxy)hydroxide phases and secondly by biological uptake. The first option is the least likely, as it has been widely observed that iodide possesses very little affinity for (oxy)hydroxid phases, and iron hydroxides in particular (Neal and Truesdale, 1976; Ullman and Aller, 1980). The second mechanism, that iodide is taken up by organisms

(photosynthetic or otherwise) in the epilimnion of the lake, appears considerably more likely. Although data of biological uptake of iodide from fresh water are scarce, such suggestions are supported by observations from marine ecosystems, where iodide is generally the preferred iodine species for uptake (Sugawara and Terada, 1967). In the marine environment it is thought that iodide is enzymatically oxidized to HOI within the cell wall (most studies are from iodine accumulating macroalgae such as *Laminaria sp.*) and only then taken into cells (Küpper et al., 1998). Also, as an alternative to algae/plankton uptake, absorption by bacteria (Rädlinger and Heumann, 2000) may also play a role in iodide immobilization and removal from the water column, as Amachi et al., (2005) have shown that bacteria isolated from marine sediments are able to absorb iodide from solution. Moreover, Fuse et al., (2003) have also demonstrated bacterial uptake and conversion of iodide to volatile organic compounds (particularly CH_2I_2). As such, it may be possible that bacteria residing in suspended particles take up iodide from the lakes water column and, on sinking of these particles, remove the iodide from the epilimnion. Such a non-photosynthetic pathway is suggested by the two winter profiles (Jan and Feb 2006), where iodide levels were generally below the detection limit in the oxic zone, despite the lake being covered with ice and snow. Biological removal is also suggested by the close relationship between total iodine and organic carbon concentrations in the sediments and, in addition, the sediment enrichment factors of >6500 . Due to the lack of data from freshwater systems it is vital for future studies to quantify iodine uptake by freshwater algae/plankton/bacteria and, most importantly, which iodine species are most susceptible to uptake.

In contrast to the epilimnion, iodide concentrations increased significantly in the hypolimnion over the summer months, when oxygen concentrations were low. The increase in iodide mobility during anoxic conditions has been recognized for a considerable amount of time, particularly in marine environments (Wong and Brewer, 1977; Luther and Cole, 1988; Žic and Branica, 2006), but has also been observed in terrestrial systems (Neal and Truesdale, 1976; Jones and Truesdale, 1984; Bird et al., 1995b; Bird and Schwartz, 1996). Despite the consensus on iodide's mobility, its source in the hypolimnic waters of freshwater lakes has not been well documented. Jones and Truesdale, (1984), for example, were not able to elucidate if the increase in iodide observed in the hypolimnion of Esthwaite lake during anoxia stemmed from the bottom sediments or from sediment (autochthonous or allochthonous) decomposition within the water column. It is clear from the depth profiles presented in Figures 3 and 4 that the increase in iodide originates from the lake bottom sediments and diffuses upwards towards the epilimnion, although a small quantity may also stem from de-iodination of organics and reduction of iodate (discussed further below). The

large variability in total iodine concentrations with sediment depth suggest that the iodide is released into the hypolimnion from a thin (few cm) surficial layer of sediment. This is in contrast to sediment from marine environments where iodine concentrations in sediments from anoxic waters show little variation with depth (Price and Calvert, 1977). The release of iodide from the sediments is then most likely from the decomposition of biological material precipitated from the overlying water column. This is further suggested by the increase in all element concentrations (and EC, data not shown) in the lower parts of the lake during the summer-autumn period.

Now that we have concluded that the iodide in the hypolimnion is mostly derived from the sediment, we can estimate some quantitative fluxes. One method to estimate the iodide flux across the sediment/water interface can be calculated as:

$$\frac{dI^-}{dt} = \frac{(dI^-_{end} - dI^-_{start})}{dz} \times \frac{1}{t} \quad (\text{Eq. 1})$$

Where:

dI^-/dt : is the flux of iodide from the sediment in $\mu\text{g m}^{-2} \text{day}^{-1}$ into the lake

$(dI^-/dz)_{end}$: is the iodide concentration gradient in $\mu\text{g m}^{-3} \text{m}^{-1}$ between the top ($z=8$ m) and bottom of the hypolimnion ($z=17$ m) at the end of any particular time period.

$(dI^-/dz)_{start}$: is the iodide concentration gradient in $\mu\text{g m}^{-3} \text{m}^{-1}$ between the top ($z=8$ m) and bottom ($z=17$ m) of the hypolimnion at the start of any particular time period.

$1/t$: is the inverse of the number of days between end and start sampling periods.

The values for the second and third terms were calculated by differentiating the line (linear) of best fit for iodide vs. depth from any selected sampling campaigns. The r^2 values for these fits ranged from 0.52-0.95 and can be found in the supplementary information Figure 1. The dI^-/dz values are plotted in Figure 8a. Note that the top of the hypolimnion varied slightly from month to month, but has been set to 8 meters. The results from this exercise can be seen in Figure 8b, and range from a strong positive flux in the May-June and September-October intervals (1.28 ± 0.3 and $1.09 \pm 0.5 \mu\text{g m}^{-2} \text{day}^{-1}$ respectively) to a strong negative flux in October-November ($-1.98 \pm 0.5 \mu\text{g m}^{-2} \text{day}^{-1}$). It is suggested that the negative flux during November is due to major mortalities in lake biology due to the cooling of the lake water associated with the oncoming winter. The falling organic debris could then scavenge iodide from the hypolimnion. It is also possible to calculate a net flux from the hypolimnion by

summing the monthly fluxes. This gives a total net flux of $1.58 \mu\text{g I}^- \text{m}^{-2} \text{day}^{-1}$ over the spring-summer-autumn period.

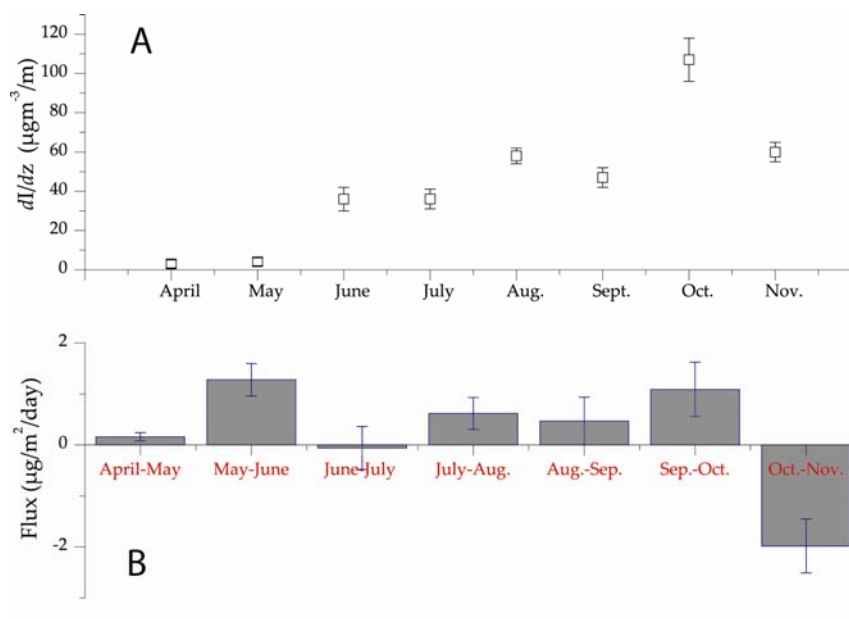


Figure 8: (a) di/dz over the spring-summer-autumn period. (b) iodide flux from the sediments and ± 1 standard error.

3.2.4.2 Iodate

The increase in iodate in the epilimnion is rather puzzling, as it is generally believed that iodate is reduced to iodide during biological reactions usually attributed to nitrate reductase (Fuge, 2005 and refs. therein). As such, we would expect a decrease in the iodate levels during the spring-summer-autumn, when biological activity is at a maximum, if similar processes were active in the lake as observed in the ocean. Photooxidation is an unlikely mechanism for the formation of iodate in the epilimnion as Wong and Cheng, (1998) have shown that organically bound iodine decays to iodide on exposure to natural sunlight. Moreover, it is also very difficult to abiologically oxidize iodide to iodate with O_2 or even more reactive oxygen species such as H_2O_2 as, as pointed out by Luther et al., (1995), it requires removal of 6 electrons and therefore must occur in a series of at least 2 electron transfer steps. Rather than oxidizing iodide to iodate, iodide is more easily oxidized to I_2 or HOI which can then attack the covalent bonds in dissolved organic material. We are only left with two possible mechanisms for the increase in iodate in the epilimnion, 1) a biologically mediated reaction, or 2) dilution of the epilimnic waters by iodate-enriched water from the inflow. In regards to the first possibility, it is unfortunate that the majority of research has focused on iodate reduction rather than iodide oxidation despite the majority of the oceans iodine existing as iodate. Recently Truesdale et al., (2001) have suggested that, based on a mass-balance of iodine speciation in the Black Sea, iodide may be oxidized by nitrifying

bacteria. In the Black Sea the pH of the seawater was too high make Mn^{4+} a thermodynamically feasible electron acceptor, whereas oxidation of iodide by nitrifying bacteria was energetically beneficial. A biological source of iodate is also consistent with our results, as the largest increase in iodate is found in the top three meters of water, which is essentially the maximum light penetration depth and also has the highest oxygen levels. However, light must not be essential for the organism as during winter when the lake was covered in snow and ice iodate could still be found down to about 13 m depth at concentrations similar to those found in the epilimnion over the summer months. As such, a rapid net production of iodate must occur during the winter turnover, although unrelated to photolytically active organisms. In regards to the favored oxidation pathway, the Eh-pH diagrams presented by Truesdale et al., (2001) suggest that a thermodynamically favorable MnO_2 -I couple may exist at the circumneutral pH's of the Mummelsee. However, we would also prefer a nitrifying reaction due to the relatively large number of electrons (six) that must be removed for iodide to be oxidised to iodate. Either way, it is unlikely that organisms exist that are specific for iodate formation due to the low levels of iodate in the lake, rather it must occur by a 'generalist' pathway where iodide can substitute for the preferred electron donor. Obviously, further work is required on the microbiology of freshwater systems in regards to iodate formation before more conclusive suggestions can be made.

The second possibility for the observed iodate increase in the epilimnion (i.e. the inflow influencing the iodate levels in the lake) is also feasible particularly as the inflow is indeed enriched in iodate compared to in the lake. The inflow enters the lake at the shallow end, and, due to its low flow rate, is rapidly warmed in the shallow water zone. The inflowing water will then be confined to the epilimnion due to the density gradient at the thermocline. The major drawback to this approach is the low inflow rate compared to the volume of the lake (residence time >450 days), however, during stratification the epilimnion is confined to the top 7 m depth and therefore contains considerably less volume than the entire lake. By using the bathymetry map in Figure 1 it is possible to calculate a residence time of water in the epilimnion (assuming epilimnion depth of 7 m and inflow rate of 6.8 l s^{-1} (Thies, 1987)) of 407 days. Therefore, over the 192-day spring-summer-autumn study period approximately 50 % of the epilimnion may have been exchanged. Thus, the increase in iodate levels in the epilimnion may be due to the iodate-enriched inflow. Note, however, that this is an upper limit as it assumes that all of the inflow flows into the epilimnion without mixing into the hypolimnion.

One of the most notable processes occurring in the Mummelsee is iodate reduction in the hypolimnion. The most likely mechanism for this is reactions with reduced species in the

water column, particularly reduced sulfur groups diffusing into, or forming in, the hypolimnion (Jia-Zhong and Whitfield, 1986). The importance of such processes increase as the lake bottom waters and sediment become progressively depleted in dissolved oxygen. Moreover, Jia-Zhong and Whitfield, (1986) found that the reaction rate of IO_3^- with HS^- was faster than the O_2 - HS^- redox couple, and as such does not require completely anoxic conditions to proceed. The reduction of iodate by reduced sulfur compounds such as sulfide has also been noted in marine environments, and particularly in biologically productive estuaries, marine enclosures and deep anoxic ocean water (Wong and Brewer, 1977; Luther and Cole, 1988; Luther and Campbell, 1991; Stipanicev and Branica, 1996). However, it is not likely that the iodate is reduced to iodide, as it must first be reduced to the highly reactive and electrophilic I^+ species, which should then rapidly react with the abundant dissolved organic material (Jia-Zhong and Whitfield, 1986). Such processes are often observed at the oxic-anoxic boundary in certain marine basins such as the Mediterranean Sea and the Black Sea (Ullman et al., 1990; Luther and Campbell, 1991). However, this cannot be a strong source of iodo-organics in the Mummelsee, as the maximum iodate concentrations in the hypolimnion just after mixing are about $0.1 \mu\text{g I}^-$.

3.2.4.3 Organically bound iodine

The presence of organically bound iodine in marine environments has been known for at least the last 30 years and is generally thought of little consequence for the ocean scale iodine cycle. However, the importance of the organo-I fraction in near shore and particularly in terrestrial environments has only recently received attention and, as shown here, is the most abundant component in the freshwater iodine cycle. As noted in the introduction, the presence of organo-I in freshwater environments has been shown in a series of one-off investigations aimed mainly at developing methods for on-line quantification of iodine species (Reifenhäuser and Heumann, 1990; Rädlinger and Heumann, 1997; Heumann et al., 1998). Neal et al., (2007) have also found indirect evidence for organo-I, with strong seasonal co-variation of total iodine (As-Ce method) with dissolved organic iodine. It has also been noted that the dominant iodine species in aerosols, rain and snow is also organic iodine, despite the traditional belief that inorganic species dominate in the atmosphere (Baker et al., 2001; Baker, 2005; Gilfedder et al., 2007c, b). We have analysed organo-I over one year in the Mummelsee and found some interesting temporal trends in the different lake compartments (stream inflow, epi- and hypolimnion). As such, analysing the temporal changes in organo-I is also an essential component in the understanding of the iodine cycle.

Organically bound iodine in the inflow had an average concentration and proportion of $1.2 \mu\text{g I}^{-1}$ and 76 % of total iodine respectively. In contrast, the lake epilimnion had an organo-I content of $1.6 \mu\text{g I}^{-1}$ and 90 % of the total iodine, respectively. Therefore, there must be net formation of organo-I in the lakes epilimnion. This was most notable over the summer-autumn months and during the winter turnover, where organo-I closely followed the total iodine curve. Such temporal changes in organo-I suggests that organisms are involved in its formation. However, while likely, this need not occur biologically, as iodate reduced to HOI by organic/biological produced (e.g. HS^{-}) reductants will react abiologically with the abundant organic matter (Francois, 1987; Reiller et al., 2006). Such a mechanism has been observed at the interface between anoxic and oxic ocean waters where considerable amounts of abundant iodate are reduced (by sulfide) to reactive intermediate iodine species that subsequently bind to organic matter (Ullman et al., 1990; Luther and Campbell, 1991). However, we generally favor the biological formation of organo-I in the Mummelsee, as 1) there is probably insufficient sulfide in the epilimnion, given the levels of oxygen (generally 100 % saturation), manganese and iron observed, for HS^{-} to act as an inorganic electron donor; 2) the known biophilic nature of iodine makes it susceptible to biological transformations. Indeed, Rädlinger and Heumann, (2000) have observed the transformation of inorganic iodide to organic forms after only 4 weeks of wastewater incubation with iodide. While such mediums as used by Rädlinger and Heumann, (2000) have significantly different microbiological communities than the Mummelsee, it demonstrates the possibility, and in fact likelihood, of microbiological iodination of organic substances. The lack of any other peaks in the anion chromatograms from both the spring inflow and the lake suggests that the iodine is bound to high molecular weight, non-ionic carbonaceous species. This is in agreement with previous studies from the Synchrotron facility, Grenoble France, on characterization of humic bound iodine isolated from groundwater (Schlegel et al., 2006). Schlegel et al., (2006) have produced the most convincing data to date that iodine is covalently bound to aromatic moieties, although earlier research had already come to similar conclusions, but with less clear evidence (Moulin et al., 2001).

In the hypolimnion organo-I levels were relatively unchanged except for during September-October 2005, January 2006, and May 2006. The noticeable decrease in organo-I during September, October, and May does not seem to be related specifically to any of the other parameters measured, and therefore a clear mechanism is difficult to specify. The most likely process is a reductive dehalogenation of the organic matter, as all occasions are associated with relatively low oxygen concentrations. It has been suggested previously that due to its strong electrophilic properties HS^{-} may be able to abstract iodine from the organic moiety

(Francois, 1987). However, the concurrent presence of other oxidizing species in the water column during August and September (O_2 , Fe^{3+} and iodate) negates an abiological mechanism, and again we must speculate about a biological process. In contrast, the lack of any significant quantities of organo-I during May 2006 could be related to abiological attack of the C-I bond due to the highly reducing nature of the bottom two meters of the lake during this time. The end products should yield iodide and organo-S compounds. The winter turnover was a unique case in that most of the iodide released from the sediments was converted to organo-I. At present we do not fully understand this process, but it must be related to oxygen introduction into the hypolimnetic waters with overturn. Perhaps the introduction of oxygen to water which contained considerable amounts of ammonium (inferred from redox profiles of O_2 , Fe and Mn; Figure 4) produced an outbreak of NH_4^+ oxidizing bacteria. In the process of NH_4^+ oxidation perhaps the I^- was also oxidized to reactive intermediate species that could then bind to the available organic matter. This is rather speculative and must be confirmed or negated in future studies on biological iodide oxidation and subsequent interactions with organics.

3.2.4.4 Sediment core

The sediment core showed some noticeable changes with depth, which is in contrast to marine sediments. Typically under reducing condition marine sediments are relatively uniform in concentration whereas under oxidizing conditions only show an enhancement in iodine concentrations near the surface (Price and Calvert, 1977; Gieskes and Mahn, 2007). Unfortunately, without better knowledge of the process that have occurred in the catchment over the last few hundred years and without more detailed chemical analysis and dating it is difficult to attribute the changes to any particular process with confidence. Speculatively, it seems possible that changes in land use within the catchment (e.g. forestry, military occupation, fires) have lead to changes in release and retention of iodine within the catchment. In-lake processes such as fluctuations in algae and bacterial populations probably also contribute to the changes observed in the sediments through time. Further investigations are planned for the future with a longer sediment core and more thorough chemical and physical analysis.

3.2.5 Conclusions

Cycling of iodine in terrestrial aquatic systems is a complex process that is sensitive to redox changes and biological activity. It has been shown here that organically bound iodine is dominant form of iodine (~90 %) in the Mummelsee, a humic rich lake in the Black Forest.

This is supported by the sediment core data where total iodine concentrations closely follow the organic carbon curve and display enrichment factors (compared to lake water) greater than 6500. However, we also observed strong iodide fluxes from the lake sediments into the hypolimnion, which was driven by low dissolved oxygen concentrations. Moreover, there was a net increase in iodate in the epilimnion, suggestive of biological oxidation of either organo-I or iodide and iodate reduction in the hypolimnion. Before a more holistic understanding of these processes can be understood it is vital for future work to elucidate specific chemical and microbiological transformations of iodine species in freshwater environments.

Acknowledgements

We would like to thank the Berg Hotel at the Mummelsee for allowing us to use their tourist boats for sampling and student Jessica Gutknecht for help with sampling on two occasions. This project was funded by the Deutsche Forschungsgemeinschaft to H. Biester under contract No. BI-734/4-5.

3.2.6 References

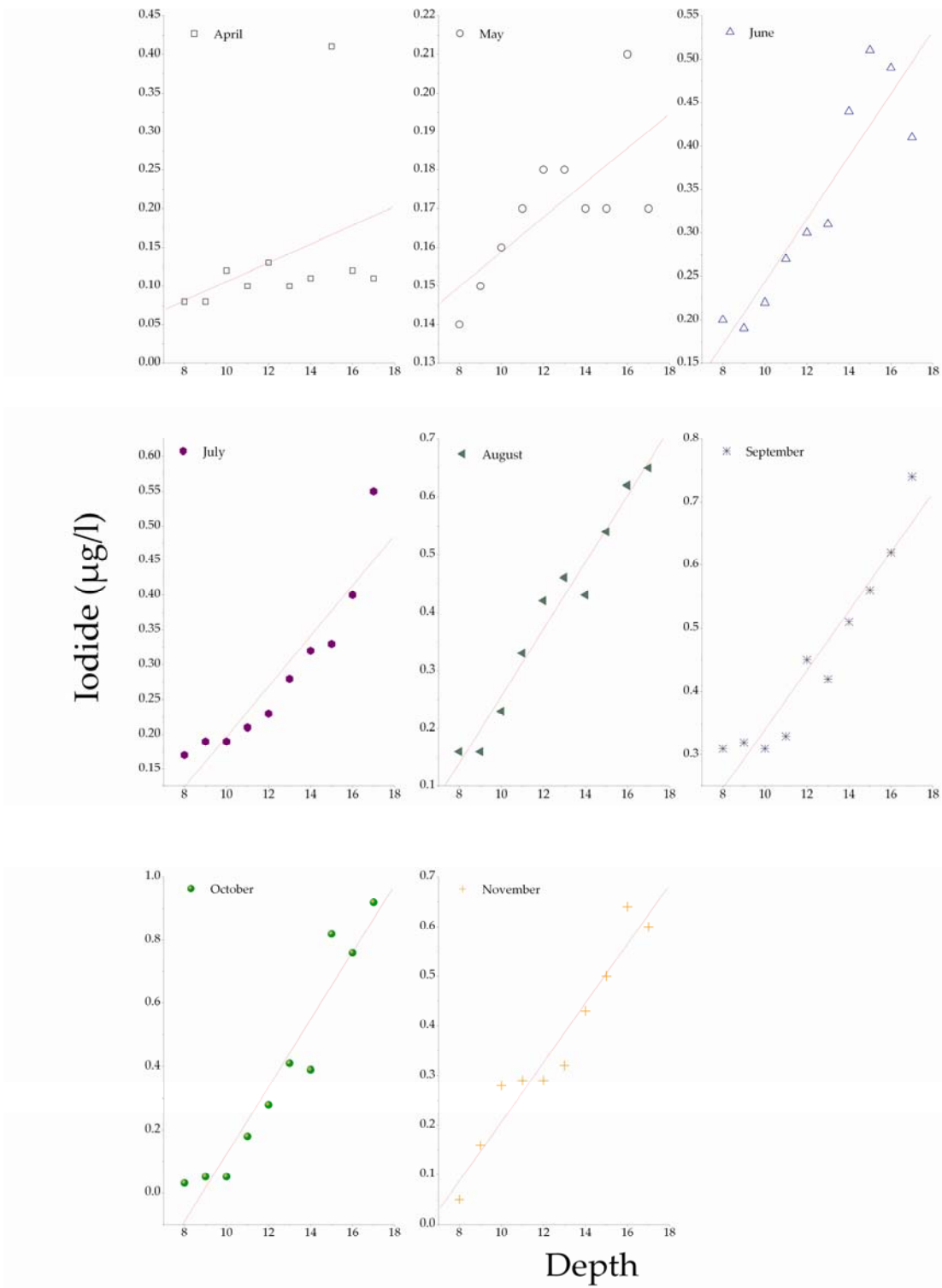
- Amachi, S., Mishima, Y., Shinoyama, H., Muramatsu, Y. and Fujii, T.: Active transport and accumulation of iodide by newly isolated marine bacteria, *Applied and Environmental Microbiology*, 71, 741-745, 2005.
- Atarashi-Andoh, M., Schnabel, C., Cook, G., MacKenzie, A.B., Dougan, A., Ellam, R.M., Freeman, S., Maden, C., Olive, V., Synal, H.A. and Xu, S.: $^{129}\text{I}/^{127}\text{I}$ ratios in surface waters of the English Lake District, *Applied Geochemistry*, 22, 628-636, 2007.
- Baker, A.R.: Marine aerosol iodine chemistry: the importance of soluble organic iodine, *Environmental Chemistry*, 2, 295-298, 2005.
- Baker, A.R., Tunnicliffe, C. and Jickells, T.D.: Iodine speciation and deposition fluxes from the marine atmosphere, *Journal of Geophysical Research*, 106, 28743-28749, 2001.
- Biester, H., Keppler, F., Putschew, A., Martinez-Cortizas, A. and Petri, M.: Halogen Retention, Organohalogens and the Role of Organic Matter Decomposition on Halogen Enrichment in Two Chilean Peat bogs, *Environmental Science and Technology*, 38, 1984 - 1991, 2004.
- Bird, G.A., Motycka, M., Rosentreter, J., Schwartz, W.J. and Vilks, P.: Behavior of ^{125}I added to limnocorrals in two Canadian Shield lakes of differing trophic states, *The Science of the Total Environment*, 166, 161-177, 1995a.
- Bird, G.A. and Schwartz, W.J.: Distribution coefficients, K_d s, for iodine in Canadian Shield lake sediment under oxic and anoxic conditions, *Journal of Environment Radioactivity*, 35, 261-279, 1996.
- Bird, G.A., Schwartz, W.J. and Rosentreter, J.: Evolution of ^{131}I from freshwater and its partitioning in simple aquatic microcosms, *The Science of the Total Environment*, 164, 151-159, 1995b.
- Campos, M.L.A.M.: New approach to evaluating dissolved iodine speciation in natural waters using cathodic stripping voltammetry and a storage study for preserving iodine species, *Marine Chemistry*, 57, 107-117, 1997.
- Chance, R., Malin, G., Jickells, T.D. and Baker, A.R.: Reduction of iodate to iodide by cold water diatom cultures, *Marine Chemistry*, 105, 169-180, 2007.

- Cook, P.L.M., Carpenter, P.D. and Butler, E.C.V.: Speciation of dissolved iodine in the waters of a humic-rich estuary, *Marine Chemistry*, 69, 179-192, 2000.
- Elderfield, H. and Truesdale, V.W.: On the biophilic nature of iodine in seawater, *Earth and Planetary Science Letters*, 50, 105-114, 1980.
- Francois, R.: The influence of humic substances on the geochemistry of iodine in nearshore and hemipelagic marine sediments, *Geochimica et Cosmochimica Acta*, 51, 2417-2427, 1987.
- Fuge, R., Soils and iodine deficiency. In: O. Selinus, Editor, *Essentials of medical geology: impacts of the natural environment on public health*, Elsevier academic press, Heidelberg (2005), pp. 417-433.
- Fuge, R. and Johnson, C.C.: The geochemistry of iodine - a review, *Environmental Geochemistry and Health*, 8, 31-54, 1986.
- Fuse, H., Inoue, H., Murakami, K., Takimura, O. and Yamaoka, Y.: Production of free and organic iodide by *Roseovarius spp.*, *FEMS Microbiology Letters*, 229, 189-194, 2003.
- Gieskes, J.M. and Mahn, C.: Halide systematics in interstitial waters of ocean drilling sediment cores, *Applied Geochemistry*, 22, 515-533, 2007.
- Gilfedder, B.S., Althoff, F., Petri, M. and Biester, H.: A thermo extraction-UV/Vis spectrophotometric method for total iodine quantification in soils and sediments, *Analytical and Bioanalytical Chemistry*, Online First, DOI: 10.1007/s00216-00007-01621-00214, 2007a.
- Gilfedder, B.S., Petri, M. and Biester, H.: Iodine and bromine speciation in snow and the effect of orographically induced precipitation, *Atmospheric Chemistry and Physics*, 7, 2661-2669, 2007b.
- Gilfedder, B.S., Petri, M. and Biester, H.: Iodine speciation in rain and snow: Implications for the atmospheric iodine sink, *Journal of Geophysical Research*, 112, doi:10.1029/2006JD007356, 2007c.
- Grüter, U.M., Kresimon, J. and Hirner, A.V.: A new HG/LT-GC/ICP-MS multi-element speciation technique for real samples in different matrices, *Fresenius Journal of Analytical Chemistry*, 368, 67-72, 2000.
- Heumann, K.G., Gallus, S.M., Rädlinger, G. and Vogl, J.: Accurate determination of element species by on-line coupling of chromatographic systems with ICP-MS using isotope dilution technique, *Spectrochimica Acta part B*, 53, 273-287, 1998.
- Jia-Zhong, Z. and Whitfield, M.: Kinetics of inorganic redox reactions in seawater: 1. The reduction of iodate by bisulphide, *Marine Chemistry*, 19, 121-137, 1986.
- Jickells, T.D., Boyd, S.S. and Knap, A.H.: Cycling in the Sargasso Sea and the Bermuda inshore waters, *Marine Chemistry*, 24, 61-82, 1988.
- Jones, S.D. and Truesdale, V.W.: Dissolved iodine species in a British freshwater systems, *Limnology and Oceanography*, 29, 1016-1024, 1984.
- Krupp, G. and Aumann, D.C.: The origin of iodine in soil: I. Iodine in rainfall over Germany, *Chemie der Erde*, 59, 57-67, 1999.
- Küpper, F.C., Schweigert, N., Ar Gall, E., Legendre, J.M., Vilter, H. and Kloareg, B.: Iodine uptake by Laminariales involves extracellular, haloperoxidase-mediated oxidation of iodide, *Planta*, 207, 163-171, 1998.
- Luther, G.W. and Campbell, T.: Iodine speciation in the water column of the Black Sea, *Deep-Sea Research*, 38, S875-S882, 1991.
- Luther, G.W. and Cole, H.: Iodine speciation in Chesapeake Bay waters, *Marine Chemistry*, 24, 315-325, 1988.
- Luther, G.W., Wu, J. and Cullen, J.B., Redox chemistry of iodine in seawater: frontier molecular orbital theory considerations. In: C.P. Huang, C.R. O'Melia and J.J. Morgan, Editors, *Aquatic Chemistry: interfacial and interspecies processes*, American Chemical Society, Washington DC (1995).
- Michel, R., Ernst, T.H., Jakob, D., Klipsch, K., Szidat, S., Synal, H.A. and Schnabel, C., Long-lived radionuclides in the environment: The case of iodine-129. *EUROSAFE*,

- http://www.eurosafe-forum.org/products/data/5/pe_235_24_1_euro2_4_2_iodine129.pdf?PHPSESSID=933dfc3de630a555e394b81657d2af29, Berlin (2002).
- Moran, J.E., Oktay, S.D. and Santschi, P.H.: Sources of iodine and iodine 129 in rivers, *Water Resources Research*, 38, 24-21 to 24-10, 2002.
- Moulin, V., Reiller, P., Amekraz, B. and Moulin, C.: Direct characterization of iodine covalently bound to fulvic acids by electrospray mass spectrometry, *Rapid Communications in Mass Spectrometry*, 15, 2488-2496, 2001.
- Neal, C., Neal, M., Wickham, H., Hill, L. and Harman, S.: Dissolved iodine in rainfall, cloud, stream and groundwater in the Plynlimon area of mid-Wales, *Hydrology and Earth System Sciences*, 11, 283-293, 2007.
- Neal, C. and Truesdale, V.W.: The sorption of iodate and iodide by riverine sediments: its implications to dilution gauging and hydrochemistry of iodine, *Journal of Hydrology*, 31, 281-291, 1976.
- Oktay, S.D., Santschi, P.H., Moran, J.E. and Sharma, P.: 129 and 127 I transport in the Mississippi River, *Environmental Science and Technology*, 35, 4470-4476, 2001.
- Price, N.B. and Calvert, S.E.: The contrasting geochemical behavior of iodine and bromine in recent sediments from Namibian shelf, *Geochimica et Cosmochimica Acta*, 41, 1769-1775, 1977.
- Rädlinger, G. and Heumann, K.G.: Determination of halogen species of humic substances using HPLC/ICP-MS coupling, *Fresenius Journal of Analytical Chemistry*, 359, 430-433, 1997.
- Rädlinger, G. and Heumann, K.G.: Transformation of iodide in natural and wastewater systems by fixation on humic substances, *Environmental Science and Technology*, 34, 3932-3936, 2000.
- Reifenhäuser, C. and Heumann, K.G.: Development of a definitive method for iodine speciation in aquatic systems, *Fresenius Journal of Analytical Chemistry*, 336, 559-563, 1990.
- Reiller, P., Mercier-Bion, F., Gimenez, N., Barre, N. and Miserque, F.: Iodination of humic acid samples from different origins, *Radiochimica Acta*, 94, 739-745, 2006.
- Schlegel, M.L., Reiller, P., Mercier-Bion, F., Barre, N. and Moulin, V.: Molecular environment of iodine in naturally iodinated humic substances: Insights from X-ray absorption spectroscopy, *Geochimica et Cosmochimica Acta*, 70, 5536-5551, 2006.
- Schwehr, K.A. and Santschi, P.H.: Sensitive determination of iodine species, including the organo-iodine, for freshwater and seawater samples using high performance liquid chromatography and spectrophotometric detection, *Analytica Chimica Acta*, 482, 59-71, 2003.
- Snyder, G. and Fehn, U.: Global distribution of 129 I in rivers and lakes: implications for iodine cycling in surface reservoirs, *Nuclear Instruments and Methods in Physics Research B*, 223-224, 579-586, 2004.
- Spokes, L.J. and Liss, P.S.: Photochemically induced redox reaction in seawater, II: nitrogen and iodine, *Marine Chemistry*, 54, 1-10, 1996.
- Stipanicev, V. and Branica, M.: Iodine speciation in the water column of the Rogoznica Lake (Eastern Adriatic Coast), *The Science of the Total Environment*, 182, 1-9, 1996.
- Sugawara, K. and Terada, K.: Iodine assimilation by a marine *Navicula* sp. and the production of iodate accompanied by the growth of the algae, *Information Bulletin on Planktology in Japan*, 213-218, 1967.
- Szidat, S., Schmidt, A., Handl, J., Jakob, D., Botsch, W., Michel, R., Synal, H.A., Schnabel, C., Suter, M., López-Gutiérrez, J.M. and Städe, W.: Iodine-129: sample preparation, quality control and analysis of pre-nuclear materials and of natural waters from Lower Saxony, Germany, *Nuclear Instruments and Methods in Physics Research B*, 172, 699-710, 2000.

- Thies, H., Limnochemische Untersuchungen an vier Karseen des Nordschwarzwalds unter Berücksichtigung von sauren Niederschlägen sowie der Makrophytenvegetation. *Limnologischen Institut Konstanz*, University of Freiburg, Freiburg (1987), pp. 1-329.
- Thies, H.: Limnochemical studies at small Black Forest Lakes (FRG) with special emphasis to acidification, *Verh. Internat. Verein. Limnol.*, 24, 806-809, 1991.
- Tian, R.C. and Nicolas, E.: Iodine speciation in the northwestern Mediterranean Sea: method and vertical profile, *Marine Chemistry*, 48, 151-156, 1995.
- Truesdale, V.W., Watts, S.F. and Rendell, A.R.: On the possibility of iodide oxidation in the near surface of the Black Sea and its implications to iodine in general oceans, *Deep-Sea Research*, 48, 2397-2412, 2001.
- Ullman, W.J. and Aller, R.C.: Dissolved iodine flux from estuarine sediments and implications for the enrichment of iodine at the sediment water interface, *Geochimica et Cosmochimica Acta*, 44, 1177-1184, 1980.
- Ullman, W.J., Luther, G.W., De Lange, G.J. and Woittiez, J.R.W.: Iodine chemistry in deep anoxic basins and overlying waters of the Mediterranean Sea, *Marine Chemistry*, 31, 153-170, 1990.
- Wong, G.T.F. and Brewer, P.G.: The marine chemistry of iodine in anoxic basins, *Geochimica et Cosmochimica Acta*, 41, 151-159, 1977.
- Wong, G.T.F. and Cheng, X.H.: Dissolved organic iodine in marine waters: determination, occurrence and analytical implications, *Marine Chemistry*, 59, 271-281, 1998.
- Wong, G.T.F. and Cheng, X.H.: The formation of iodide in inshore waters from the photochemical decomposition of dissolved organic iodine, *Marine Chemistry*, 74, 53-64, 2001.
- Wuilloud, R.G., de Wuilloud, J.C.A., Vonderheide, A.P. and Caruso, J.A.: Determination of iodinated phenol species at parts-per-trillion concentration levels in different water samples by solid-phase microextraction/offline GC-ICP-MS, *Journal of Analytical Atomic Spectroscopy*, 18, 1119-1124, 2003.
- Žic, V. and Branica, M.: The distributions of iodate and iodide in Rogoznica Lake (East Adriatic Coast), *Estuarine, Coastal and Shelf Science*, 66, 55-66, 2006.

Supplementary information



Supplementary Figure 1: Regression of iodide vs. depth.