Biogeosciences Discuss., 5, 25–64, 2008
www.biogeosciences-discuss.net/5/25/2008/

Biogeosciences
Discussions

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

B. S. Gilfedder[1], M. Petri[2], and H. Biester[1]

[1]Institut für Umweltgeochemie, Neuenheimer Feld 236, 69120 Heidelberg, Germany
[2]Zweckverband Bodensee-Wasserversorgung, Betriebs- und Forschungslabor, Süßenmühle 1, 78354 Sipplingen, Germany

Received: 28 November 2007 – Accepted: 2 December 2007 – Published: 4 January 2008

Correspondence to: B. S. Gilfedder (benjamin.gilfedder@ugc.uni-heidelberg.de)

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 $1.93\pm0.3\,\mu\mathrm{g\,l}^{-1}$. Organo-I was the dominant species in the lake, making up on average 85±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. $11.8\pm1.7\,\mathrm{mg\,kg}^{-1}$). 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 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 and perhaps biological activity were also important, particularly in the hypolimnion during stratification.

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 (0.3–20 μg 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 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 ngl^{-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 mgl^{-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.

1.1 Study site and methods

The Mummelsee is a small humic (DOC ~7 mgl^{-1}) cirque lake located in the northern part of the Black Forest, Germany, at 1036 m a.s.l. (Fig. 1). The lake has a maximum depth of 17 m, surface area of 3.7 ha and volume of 277 500 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 μs cm^{-1}) values. Our measurements have shown that the lake has, to a large degree, recovered since this time with EC dropping to ~33 μs cm^{-1} and pH ranging from 6–7.

1.2 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 μm) and dissolved (<0.45 μm) 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 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. Org-I=total I–(I$^-$+ 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 ngl^{-1} and each sample has a run-time of only 12 min (Fig. 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 μg l^{-1} concentration level, gave a standard deviation (STD) of ±0.006 μg l^{-1} and a relative standard deviation (RSD) of 4 % whereas iodide, at a concentration level of 0.06 μg l^{-1} gave STD of 0.005 μg 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±1.3 μgl^{-1}), and iodide (9.0±1.1 μg l^{-1}). All of our values were consistently within the error given in the certificate and averaged 9.7 μg l^{-1} for total iodine and average 9.4±0.4 μg 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 available in the certificate were within 10% (Fe−1%, Mn 5%, Al 9.5%, Si not given) of the certificate value.

1.3 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 "H_2S" 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 N_2 atmosphere and transferred into 50 ml Falcon^{TM} 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 Ce^{4+} by As^{3+} and loss of the yellow coloured Ce^{4+} 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 Fig. 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 ^{210}Pb using the constant rate of supply model. The ^{214}Am 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 ^{214}Am peak also agreed perfectly with the first ^{137}Cs 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.

2 Results

2.1 Temperature profiles and stratification

The temperature depth profiles from the Mummelsee displayed patterns typical for lakes in temperate environments (Figs. 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 pe ∼0 and a strong "H_2S" smell. This is commensurate with depth profiles for redox sensitive elements Fe and Mn, which dramatically increase in concentration from $Fe<100\,\mu g\,l^{-1}$ and $Mn<10\,\mu g\,l^{-1}$ in the epilimnion to $Fe>2\,mgl^{-1}$ and $Mn>80\,\mu g\,l^{-1}$ 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.

2.2 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 (Figs. 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 $1.88\pm0.06\,\mu g\,l^{-1}$ and iodide and iodate where approximately equal in concentration (∼$0.1\,\mu g\,l^{-1}$). Organically bound iodine (organo-I) was by far the most abundant iodine species averaging $1.68\,\mu g\,l^{-1}$, which is about 90% of the total iodine (Fig. 3). Organically bound iodine levels were relatively uniform over the spring-summer period (av. $1.6\pm0.15\,\mu g\,l^{-1}$: 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 (Fig. 3). There was also a decline in hypolimnic org-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 $0.18\,\mu g\,l^{-1}$) 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 ∼$0.15\,\mu g\,l^{-1}$ after the spring turnover 2005 to $0.8\,\mu g\,l^{-1}$ 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, Mn_{part}/Mn_{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 $<0.1\,\mu g\,l^{-1}$ 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 (Fig. 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. $>0.45\,\mu m$), 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.

2.3 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 (Fig. 4). In the well-mixed layer, iodate (0.14 μg l^{-1}) and organo-I (~1.7 μg 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±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 μg l^{-1}. The highly reducing nature of this zone is also shown by little difference between particulate and dissolved Fe (2 mgl^{-1}) and Mn (100 μg l^{-1}) levels. Qualitatively, we also noticed a strong "H_2S" 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, with the bottom 2 m remaining highly anoxic and rich in iodide (3.24 μg 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 February also contained nearly no organically bound iodine, accounting for only 2–3% of the total.

2.4 Inflow

The Mummelsee has only one small inflow; a spring located 2 m from the lake's north-eastern 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±0.28 μg l^{-1} and apart from one high concentration in spring 2005, levels were relatively uniform throughout the year (Fig. 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; Fig. 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.

2.5 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±1.7 mg kg^{-1}, but were quite variable with depth and closely followed the organic-C curve (Fig. 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 week (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 (Fig. 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 (Fig. 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.

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 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 μg l^{-1}, which is very similar to our average value of 1.92 μg 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 m a.s.l., 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 μg 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 μg 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 μg 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 μg l^{-1}. Snow samples from the Mummelsee's surface taken during winter (Gilfedder et al., 2007b) had nearly identical concentrations (1.84±0.17 μg 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 μg l^{-1} and median of 10.2 μg 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 μg 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.

3.1 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 an 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 alterative 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 (January and February, 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 Figs. 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 sediments, we can estimate some quantitative fluxes. One method to estimate the iodide flux across the sediment/water interface can be calculated as:

$$\frac{dI^-}{dt} = \frac{(dI^-\text{end} - dI^-\text{start})}{dz} \times \frac{1}{t} \tag{1}$$

Where:

dI^-/dt : is the flux of iodide from the sediment in μg m^{-2}day^{-1} into the lake

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

$(dI^-/dz)_{\text{start}}$: is the iodide concentration gradient in μg m^{-3}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 http://www.biogeosciences-discuss.net/5/25/2008/bgd-5-25-2008-supplement. Fig. 1. The *dI/dz* values are plotted in Fig. 8a. Note that the top of the hypolimnion varied slightly from month to month, but has been set to 8 m. The results from this exercise can be seen in Fig. 8b, and range from a strong positive flux in the May–June and September–October intervals (1.28±0.3 and 1.09±0.5 μg m^{-2}day^{-1} respectively) to a strong negative flux in October-November (−1.98±0.5 μg m^{-2}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 μg I$^-$m^{-2}day^{-1} over the spring-summer-autumn period.

3.2 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 references 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 by oxidized by nitrifying bacteria. In the Black Sea the pH of the seawater was too high make Mn^{4+} a thermodynamically feasible electron accepter, 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 exists 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 Fig. 1 it is possible to calculate a residence time of water in the epilimnion (assuming epilimnion depth of 7 m and inflow rate of $6.8\,\mathrm{l\,s^{-1}}$ 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 $\mu g\,l^{-1}$.

3.3 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 $\mu g\,l^{-1}$ and 76% of total iodine respectively. In contrast, the lake epilimnion had an organo-I content of 1.6 $\mu g\,l^{-1}$ 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 were 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 mater, 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 hypolimnic 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; Fig. 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.

3.4 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 seams 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.

4 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 were 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 J. Gutknecht for help with sampling on two occasions. B. S. Gilfedder would like to thank H. Thies for sending his diplome thesis and other relevant papers on element cycling in lakes from the Black Forest. C. Schultz is also thanked for help with the ICP-OES measurements. This project was funded by the Deutsche Forschungsgemeinschaft to H. Biester under contract No. BI-734/4-5.

References

Amachi, S., Mishima, Y., Shinoyama, H., Muramatsu, Y., and Fujii, T.: Active transport and accumulation of iodide by newly isolated marine bacteria, Appl. Environ. Microbiol., 71, 741–745, 2005.

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}I/^{127}I ratios in surface waters of the English Lake District, Appl. Geochem., 22, 628–636, 2007.

Baker, A. R.: Marine aerosol iodine chemistry: the importance of soluble organic iodine, Environ. Chem., 2, 295–298, 2005.

Baker, A. R., Tunnicliffe, C., and Jickells, T. D.: Iodine speciation and deposition fluxes from the marine atmosphere, J. Geophys. Res., 106, 28 743–28 749, 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, Environ. Sci. Technol., 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, Sci. Total Environ., 166, 161–177, 1995a.

Bird, G. A. and Schwartz, W. J.: Distribution coefficients, Kds, for iodine in Canadian Shield lake sediment under oxic and anoxic conditions, J. Environ. Radioactiv., 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, Sci. Total Environ., 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, Mar. Chem., 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, Mar. Chem., 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, Mar. Chem., 69, 179–192, 2000.

Elderfield, H. and Truesdale, V. W.: On the biophilic nature of iodine in seawater, Earth. Planet. Sc. Lett., 50, 105–114, 1980.

Francois, R.: The influence of humic substances on the geochemistry of iodine in nearshore and hemipelagic marine sediments, Geochim. Cosmochim. Ac., 51, 2417–2427, 1987.

Fuge, R.: Soils and iodine deficiency, in: Essentials of medical geology: impacts of the natural environment on public health, edited by: O. Selinus, Elsevier Academic Press, Heidelberg, pp. 417–433, 2005.

Fuge, R. and Johnson, C. C.: The geochemistry of iodine – a review, Environ. Geochem. Hlth, 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 Microbiol. Lett., 229, 189–194, 2003.

Gieskes, J. M. and Mahn, C.: Halide systematics in interstitial waters of ocean drilling sediment cores, Appl. Geochem., 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, Anal. Bioanal. Chem., 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, Atmos. Chem. Phys., 7, 2661–2669, 2007b.

Gilfedder, B. S., Petri, M., and Biester, H.: Iodine speciation in rain and snow: Implications for the atmospheric iodine sink, J. Geophys. Res., 112, D07301, 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 J. Anal. Chem., 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, Spectrochim. Acta B, 53, 273–287, 1998.

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.

Jia-Zhong, Z. and Whitfield, M.: Kinetics of inorganic redox reactions in seawater: 1. The reduction of iodate by bisulphide, Mar. Chem., 19, 121–137, 1986.

Jickells, T. D., Boyd, S. S., and Knap, A. H.: Cycling in the Sargasso Sea and the Bermuda inshore waters, Mar. Chem., 24, 61–82, 1988.

Jones, S. D. and Truesdale, V. W.: Dissolved iodine species in a British freshwater systems, Limnol. Oceanogr., 29, 1016–1024, 1984.

Krupp, G. and Aumann, D. C.: The origin of iodine in soil: I. Iodine in rainfall over Germany, Chem. 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 Res., 38, S875–S882, 1991.

Luther, G. W. and Cole, H.: Iodine speciation in Chesapeake Bay waters, Mar. Chem., 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:Aquatic Chemistry: interfacial and interspecies processes, edited by: Huang, C. P., O'Melia, C. R., and Morgan, J. J., American Chemical Society, Washington DC, 1995.

Michel, R., Ernst, T. H., Jackob, 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 Resour. Res., 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 Commun. Mass Sp., 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, Hydrol. Earth Syst. Sci., 11, 283–293, 2007, http://www.hydrol-earth-syst-sci.net/11/283/2007/.

Neal, C. and Truesdale, V. W.: The sorption of iodate and iodide by riverine sediments: its implications to dilution gauging and hydrochemistry of iodine, J. Hydrol., 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, Environ. Sci. Technol., 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, Geochim. Cosmochim. Ac., 41, 1769–1775, 1977.

Rädlinger, G. and Heumann, K. G.: Determination of halogen species of humic substances using HPLC/ICP-MS coupling, Fresenius J. Anal. Chem., 359, 430–433, 1997.

Rädlinger, G. and Heumann, K. G.: Transformation of iodide in natural and wastewater systems by fixation on humic substances, Environ. Sci. Technol., 34, 3932–3936, 2000.

Reifenhäuser, C. and Heumann, K. G.: Development of a definitive method for iodine speciation in aquatic systems, Fresenius J. Anal. Chem., 336, 559–563, 1990.

Reiller, P., Mercier-Bion, F., Gimenez, N., Barre, N., and Miserque, F.: Iodination of humic acid samples from different origins, Radiochim. 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, Geochim. Cosmochim. Ac., 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, Anal. Chim. 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, Nucl. Instrum. Meth. B, 223–224, 579–586, 2004.

Spokes, L. J. and Liss, P. S.: Photochemically induced redox reaction in seawater, II: nitrogen and iodine, Mar. Chem., 54, 1–10, 1996.

Stipanicev, V. and Branica, M.: Iodine speciation in the water column of the Rogoznica Lake (Eastern Adriatic Coast), Sci. Total Environ., 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., Jackob, 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, Nucl. Instrum. Meth. B, 172, 699–710, 2000.

Thies, H.: Limnochemische Unterschungen an vier Karseen des Nordschwarzwalds unter Berücksichtigung von sauren Niederschlägen sowie der Makrophytenvegetation, Limnologischen Institut Konstanz, University of Freiburg, Freiburg , pp. 1–329, 1987.

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, Mar. Chem., 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 Res., 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, Geochim. Cosmochim. Ac., 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, Mar. Chem., 31, 153–170, 1990.

Wong, G. T. F. and Brewer, P. G.: The marine chemistry of iodine in anoxic basins, Geochim. Cosmochim. Ac., 41, 151–159, 1977.

Wong, G. T. F. and Cheng, X. H.: Dissolved organic iodine in marine waters: determination, occurrence and analytical implications, Mar. Chem., 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, Mar. Chem., 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, J. Anal. Atom. Spectrom., 18, 1119–1124, 2003.

Table 1. Precision of iodine speciation by IC-ICP-MS. All concentrations in μg 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

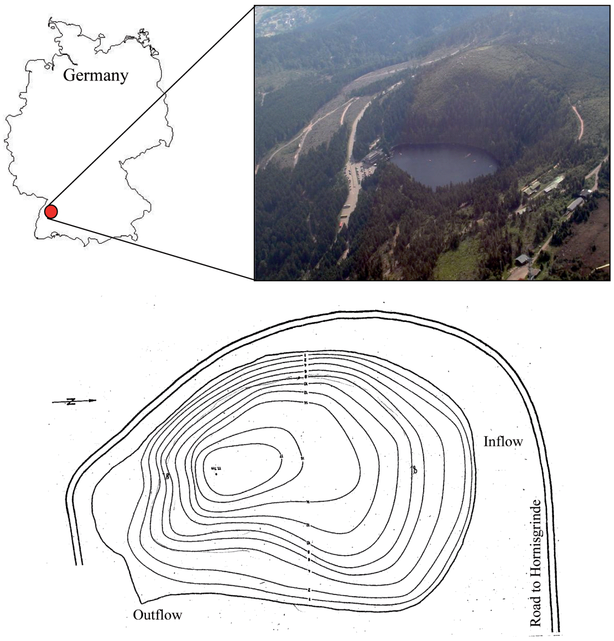

Fig. 1. The Mummelsee study site. Maximum width of the lake is 180 m and max length is 280 m. Depth contours every 2 m. The bathymetry map is oriented the same as the insert photo.

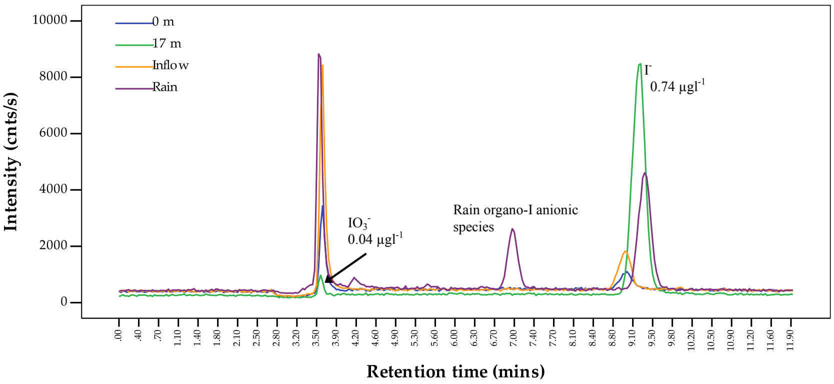

Fig. 2. IC-ICP-MS iodine speciation chromatograms of samples from 0 m and 17 m depth, the spring inflow, and a rain sample collected on the shore of the lake. The rain sample is from the data in Gilfedder et al. (2007c).

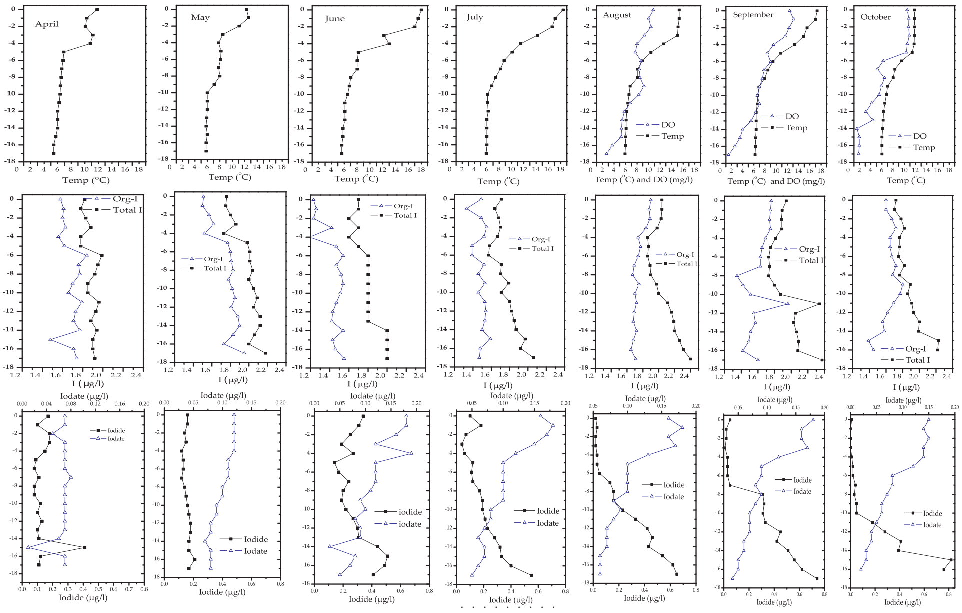

Fig. 3a. Depth profiles for the Mummelsee. April 2005 to October 2005. f=filtered, nf=not filtered.

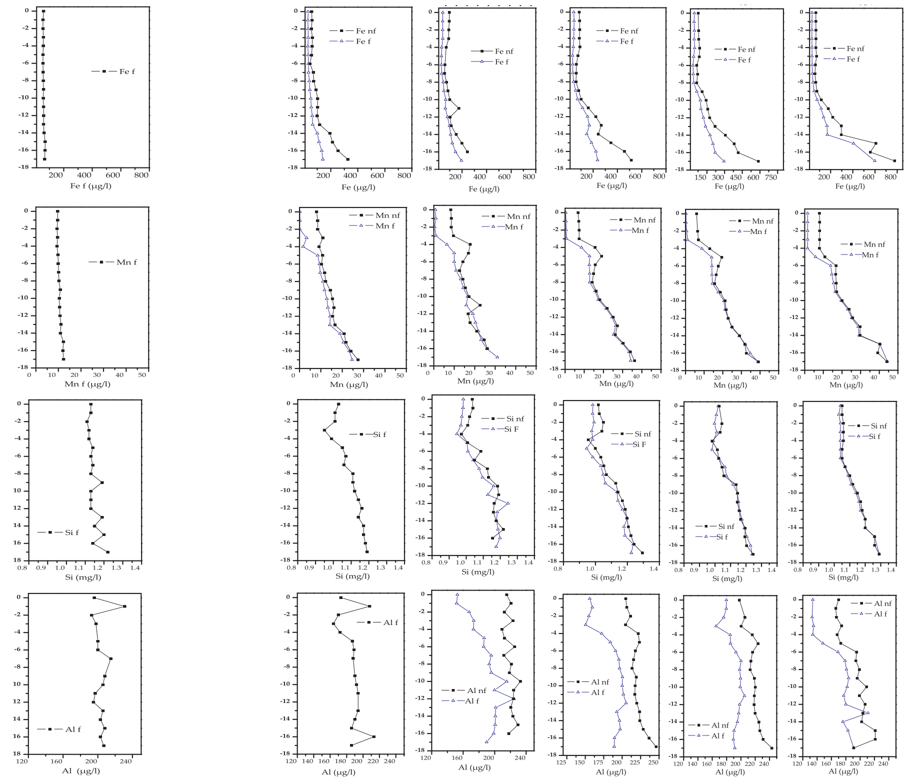

Fig. 3b. Continued.

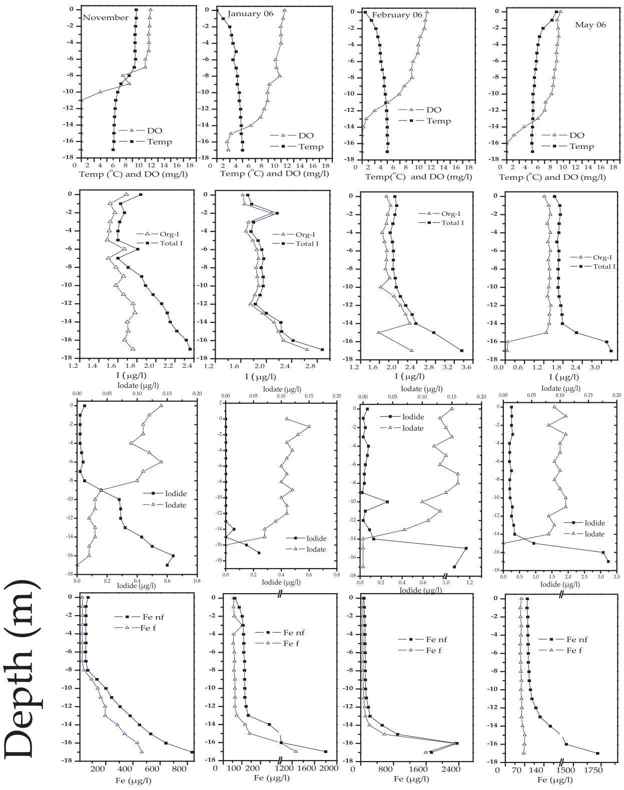

Fig. 4a. Depth profiles for the Mummelsee. November 2005 to May 2006. f=filtered, nf=not filtered.

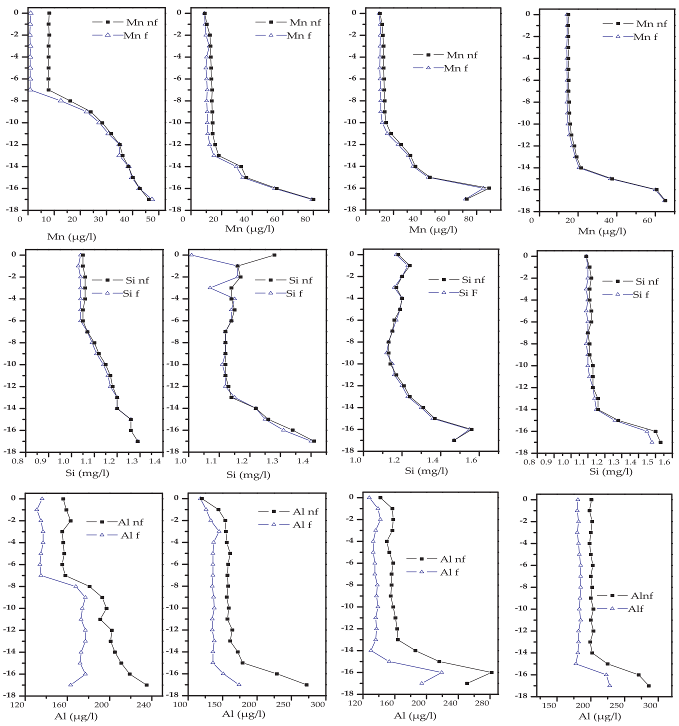

Fig. 4b. Continued.

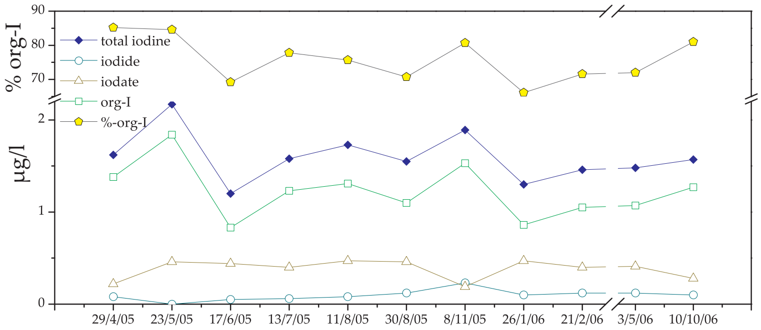

Fig. 5. Total iodine concentrations and speciation in the spring inflow.

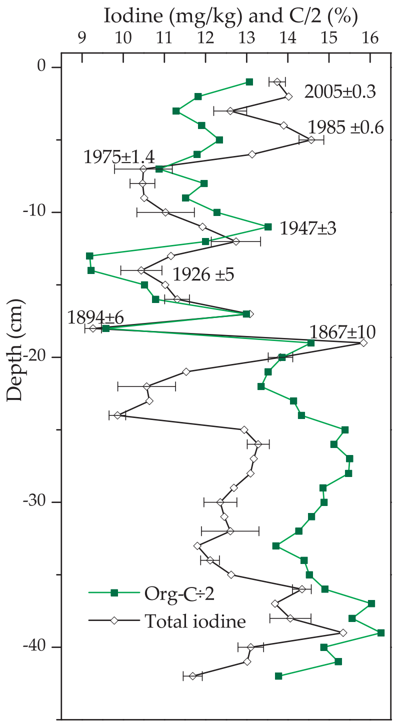

Fig. 6. Total iodine and organic carbon in a 42 cm sediment core from the Mummelsee. Note that organic carbon concentrations are divided by 2 to allow better comparison. Error bars on total iodine represent 1σ of triplicate analysis.

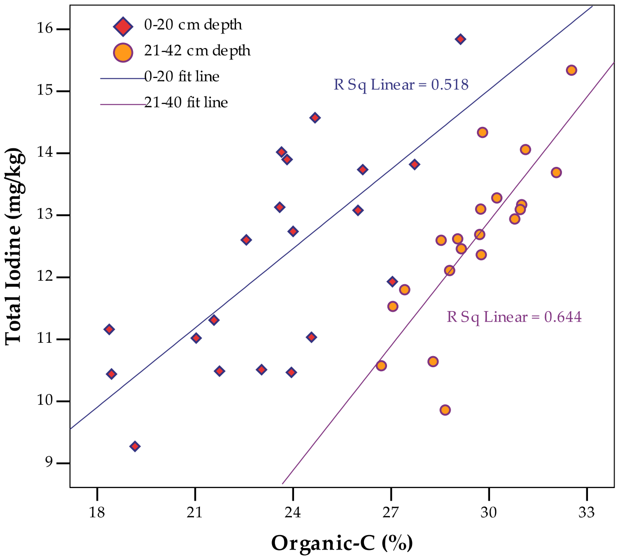

Fig. 7. Total iodine vs. organic-C concentrations in sediments from 0–20 cm and 21–42 cm depth.

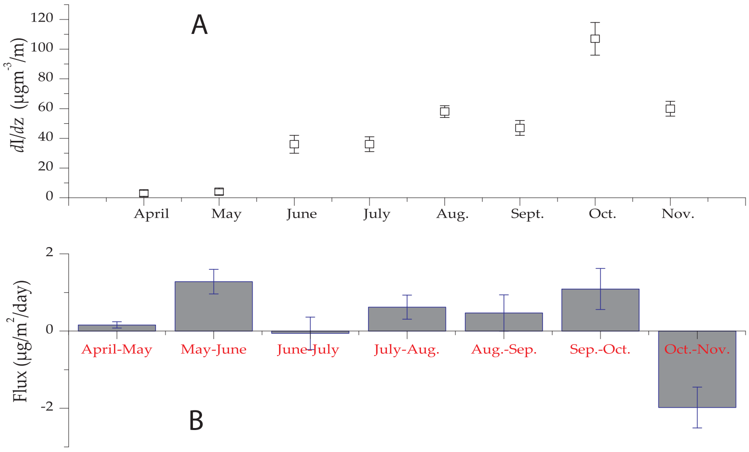

Fig. 8. (a) *dI/dz* over the spring-summer-autumn period in the hypolimnion **(b)** iodide flux from the sediments and ±1 standard error.