

A comparison of methyl iodide emissions from seawater and wet depositional fluxes of iodine over the southern North Sea

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ABSTRACT

The results of measurements of sea-to-air fluxes of methyl iodide and air-to-sea wet depositional fluxes of iodide and iodate over the southern North Sea are reported. The estimated average annual flux of methyl iodide out of the southern North Sea is 8×10^5 moles yr^{-1} while the iodine deposition flux, based on average rainwater concentrations, is 6×10^5 moles yr^{-1} . Both emission fluxes of methyl iodide and deposition fluxes of total iodine show a modest seasonality with minimum fluxes in winter. The average concentration of iodine in the rainwater samples ($n = 40$) over a one year period was $6.8 + 7.5$ nM for total iodine, $3.1 + 2.7$ nM for iodate and $3.7 + 6.6$ nM for iodide. There is no evidence of seasonality in the iodide/iodate ratio in rainwater over the year.

1. Introduction

The atmosphere represents a major but poorly understood route of iodine transport from the relatively iodine rich oceans to the iodine deficient land (Fuge and Johnson, 1986). Although there are anthropogenic atmospheric iodine sources these appear to be small in comparison to the natural marine source (Solomon et al., 1994). This sea to land iodine transport has implications for public health via goitre, a human disease of iodine deficiency. Furthermore it has been suggested that atmospheric iodine chemistry may play several important roles in oxidation reactions and ozone loss (Chameides and Davis, 1980; Sturges and Barrie, 1988; Jenkin et al., 1985; Chatfield and Crutzen, 1990; Luther et al., 1995; Solomon et al., 1994). It has also been suggested that iodine may also play a role in dimethyl sulphide (DMS) oxidation, but this is now considered unlikely (Chatfield and Crutzen, 1990; Barnes et al., 1991).

The transfer of iodine from the oceans to the atmosphere is thought to occur primarily through the volatilisation of methyl iodide, although other

organic iodine species may contribute up to 50% of the total flux (Lovelock et al., 1973; Singh et al., 1983; Klick and Abrahamsson, 1992; Moore and Tokarczyk, 1992, 1993). The emission of methyl iodide appears to be under biological control and associated with marine seaweeds, phytoplankton and possibly bacteria (Lovelock, 1975; Liss et al., 1994a; Manley, 1994; Nightingale et al., 1995), although a photochemical mechanism may also be important (Moore and Zafiriu, 1994). Total methyl iodide fluxes from the oceans to the atmosphere have been estimated at about 1 Mtons yr^{-1} (Chameides and Davis, 1980; Reifenhauer and Heumann, 1992).

Despite the recent research effort directed at the atmospheric cycling and transformations of methyl iodide in particular, the atmospheric cycling of iodine is still rather poorly understood and the available data are inadequate to allow a quantitative description of the process involved. This arises in part because the biological processes that appear to be driving atmospheric iodine cycling are themselves variable in space and time. Further problems arise because previous studies have tended to focus on parts of the iodine cycle rather than trying to view the emission, transformation and deposition of iodine as a single entity.

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In this contribution, we present new data on the emission of methyl iodide from the southern North Sea and compare this with estimates of iodine wet deposition fluxes. Since other organo-iodine compounds may be emitted from seawater, these emission estimates are likely to be lower limits. We use this information to try to arrive at a more comprehensive understanding of iodine cycling on a regional scale.

2. Experimental methods

2.1. Methyl iodide emissions

Methyl iodide concentrations in surface seawater were measured on a regular cruise track (Fig. 1) over a 2-week period of every month from January to September 1989 as part of the NERC North Sea Project (Liss et al., 1994a). All 772 samples used in this study were collected from between 0.5- and 3-m depth using 10 l Go-Flo® sampling bottles and analysed within fifteen

minutes of collection. Delays in analysis have been observed to result in increases in methyl iodide concentrations of 0–15 % h^{-1} (Nightingale, 1991). Samples were analysed using a purge and cryo-trap electron capture gas chromatography technique (Nightingale, 1991; Krysell and Nightingale, 1994). The detection limit of this system was 0.02 ng l^{-1} , analytical precision was 5% and total accuracy of measurements estimated to be 15%, the accuracy being mainly governed by the reproducibility in preparing liquid standards. In this paper we consider the net sea-to-air methyl iodide flux from seawater calculated using the approach of Liss and Slater (1974), with a wind speed dependent gas exchange transfer velocity (Liss and Merlivat, 1986). As discussed later, we consider both instantaneous and climatologically averaged winds for this calculation.

Although no measurements of atmospheric methyl iodide were made on the ship, results from a site on the North Norfolk coast showed summer concentrations of typically 2 pptv falling below detection limits (about 0.5 pptv, Oram, personal communication) during the remainder of the year (Oram and Penkett, 1994). There is no atmospheric data available prior to June 1989 so, in order to calculate net sea-to-air fluxes, we have assumed the following atmospheric methyl iodide concentration cycle based on the data of Oram and Penkett (1994): February/March 0.5 pptv, April 1 pptv, May to August 2 pptv, September/October 1 pptv. The magnitude of the sea-to-air flux is not particularly sensitive to these assumed concentrations; a zero atmospheric methyl iodide concentration increases the flux by about 5%. Such uncertainties are small compared to those arising from the unresolved uncertainties in the relationship between gas exchange rates and wind speed (Wanninkhof, 1992).

2.2. Iodine deposition fluxes

We estimate wet deposition directly based on rain samples collected either at sea, as part of the North Sea project cruises (Rendell et al., 1993), or at Mannington Hall (Kane et al., 1994) in North Norfolk (Fig. 1). Rainwater samples were collected over one year from March 1989 to February 1990, i.e., the same time period as the methyl iodide measurements in seawater. We have combined the data from the two rain sampling sites to maximise the available information. Kane et al. (1994)

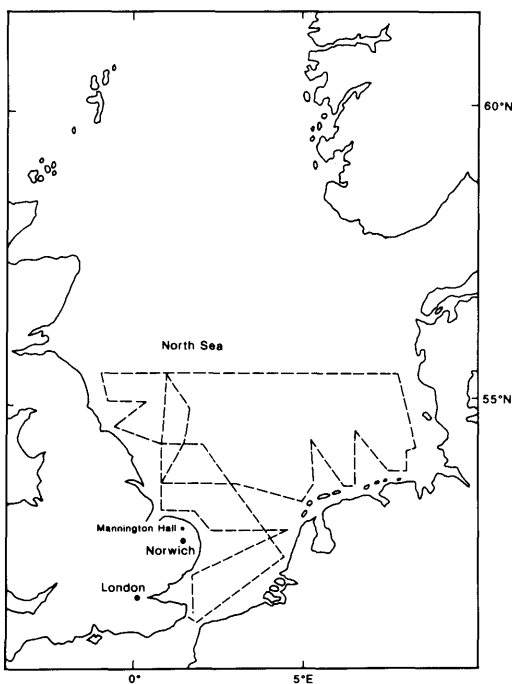


Fig. 1. Map of southern North Sea showing cruise track for the North Sea Project on which all shipboard samples were collected. Also shown is the North Norfolk site at Mannington Hall.

suggest that for most parameters the two data sets are indistinguishable.

The rain samples were archived by freezing, a procedure which is in general adequate to preserve both total iodine concentrations and redox speciation (Campos et al., in press). This is consistent with theoretical descriptions of very slow iodide chemical oxidation kinetics (Luther et al., 1995). The rain samples collected at sea are all event samples, those from the North Norfolk site are a mixture of event and weekly composite samples. Kane et al. (1994) noted that for major ions and trace metals in rainwater there was no difference between the average concentrations in event and weekly samples and we assume the same to be true for iodine. Samples were thawed and filtered ($0.2 \mu\text{m}$ cellulose acetate) prior to analysis.

Iodine speciation in the rainwater was determined electrochemically using square wave voltammetry on a PAR 273 instrument with a PAR 303A electrode. Total iodine is defined here as the sum of iodide and iodate, with other iodine species in rainwater assumed to be of negligible concentration. The electrochemical method of Luther et al. (1988) for iodide in seawater was adapted to rainwater using a borate buffer as a support electrolyte. Total iodine was determined after reduction of iodate with ascorbic acid. These adaptations minimise interferences and reduce reagent contamination, thereby lowering the detection limit for iodide by at least a factor of 3 over existing methods. A brief description of the analytical procedure is given below, and full details will be published elsewhere.

2.2.1. Procedure. 10 ml of rainwater sample, $100 \mu\text{l}$ 1 M borate buffer and $75 \mu\text{l}$ 0.2% Triton-X-100 were added to the voltammetric cell. The solution was then purged with argon for 10 min, and iodide was preconcentrated onto the mercury drop at a potential of -0.15 V for 1 to 5 min, depending on the iodide concentration. After deposition, the potential was scanned from -0.15 to -0.8 V and the resulting current peak at -0.37 V versus Ag/AgCl was measured. Following the quantification of iodide by standard additions of potassium iodide, iodate was reduced to iodide by the addition of $50 \mu\text{l}$ 0.1 M ascorbic acid and $50 \mu\text{l}$ 6 M hydrochloric acid. After 1 min, the sample was neutralised with ammonia, and the analysis, including standard additions, repeated to determine the total iodine concentration. Iodate

was determined by difference. The reduction step has been shown to be 100% efficient (Campos, unpublished data). Samples were analysed in duplicate with a typical precision of $\pm 10\%$ with total reagent and sampling blanks of about $0.15 \pm 0.05 \text{ nM}$. In the absence of suitable certified reference material for rainwater iodine, the accuracy of the method cannot be addressed directly. However, at the higher concentrations found in seawater we have demonstrated that the method gives results consistent with published data (Campos et al., in press) and hence is likely to be accurate.

To estimate deposition we consider only wet deposition since the iodine in aerosols arises from gas to particle conversions and is therefore assumed to be associated with the fine aerosol fraction. This fine fraction is subject to relatively inefficient dry deposition (Jickells, 1995 and references therein) and hence we anticipate dry deposition to be less than wet deposition. The sensitivity of our final conclusions to this assumption are considered later.

3. Results

The measured rainwater concentrations and the iodine redox speciation are presented in Fig. 2. The direct contribution of marine dissolved iodide and iodate to the rains via seaspray is small. Based on sodium concentrations in the rain samples, the seawater iodine contribution is generally $<5\%$ and between 5 and 20% for only 5 samples out of 40. There is no correlation between iodine and sodium concentrations in rain samples. Thus we conclude that seaspray sources for the rainwater iodine are minor. Iodine was enriched in the rainwaters by factors of up to 10^4 , compared to bulk seawater. Since iodine enrichment in seasurface microlayer samples appear to be small (Chapman and Liss, 1981) this is also considered to be a minor source of iodine in the rainwater. We believe, in agreement with previous studies (see introduction), that marine biogenic gases are the primary sources of iodine to the atmosphere.

The two particularly high rainwater iodine values were observed in samples collected on 30 September and 17–24 November 1989. We have no reason to believe that either of these samples are contaminated. The high iodine value in September

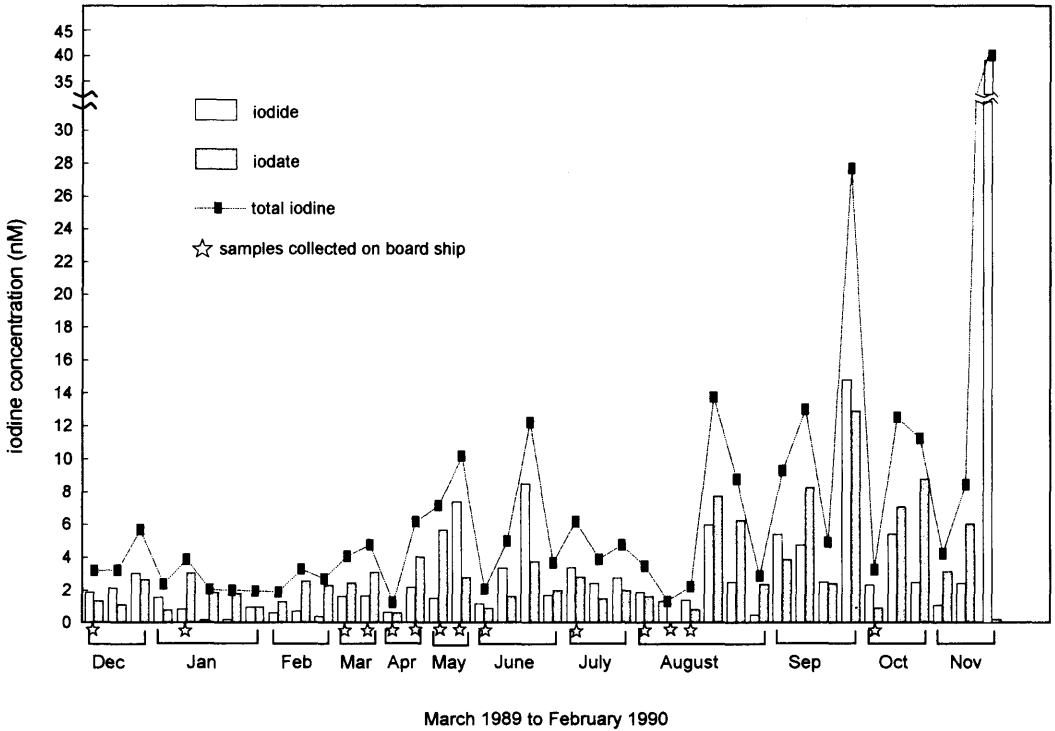


Fig. 2. Total iodine, iodide and iodate concentrations in rainwater samples from the southern North Sea region collected at the coastal site and on board ship from March 1989 to February 1990. Note the change of scale on the y-axis and the non-linear scale on the x-axis.

was associated with transport from the north, based on air parcel back trajectories. Additionally, exceptionally high (ten times average) methyl iodide concentrations were observed in surface seawater off the Norfolk coast at this time (Nightingale, 1991), suggesting that local sources of methyl iodide may be particularly important. The week of 17–24 November was characterized by low rainfall and thus this high concentration may reflect efficient wash out in a small rain event. This sample was again associated with northerly air parcel back trajectories, which are relatively rare in this region (Yaaqub et al., 1991). We suggest that these very high values could be characteristic of at least some air masses associated with northerly transport, allowing maximum time over the sea and presumably maximum time for the samples to accumulate marine biogenic iodine. Occasional high methyl iodide air concentrations

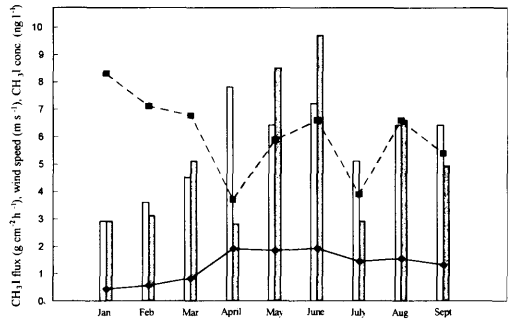


Fig. 3. The sea-to-air flux of methyl iodide, February 1989 to October 1989. ■ Mean wind speed at sampling sites m s^{-1} ; ♦ mean surface seawater concentrations of methyl iodide (ng l^{-1}). Solid bars are mean methyl iodide fluxes ($\text{g cm}^{-2} \text{h}^{-1}$) based on windspeed at sampling sites and open bars are mean monthly methyl iodide fluxes ($\text{g cm}^{-2} \text{h}^{-1}$) based on 25-year climatological average wind speeds for the southern North Sea.

Table 1. *Southern North Sea iodine budget*

Emission	
southern North Sea area	$2.3 \times 10^{11} \text{ m}^2$
average methyl iodide flux ^{a)}	$5.6 \times 10^{-12} \text{ g cm}^{-2} \text{ h}^{-1}$ ($3.4 \times 10^{-6} \text{ moles m}^{-2} \text{ yr}^{-1}$)
methyl iodide emission flux	$2.3 \times 10^{11} \times 3.4 \times 10^{-6} = 8 \times 10^5 \text{ moles yr}^{-1}$
Deposition	
rain fall over southern N. Sea ^{b)}	400 mm yr^{-1} (0.4 m yr^{-1})
average total iodine in rainwater	$6.8 \times 10^{-9} \text{ moles l}^{-1}$ ($6.8 \times 10^{-9} \text{ moles } 10^3 \text{ m}^3$)
total iodine deposition flux	$2.3 \times 10^{11} \times 0.4 \times 6.8 \times 10^{-9} \times 10^3 = 6 \times 10^5 \text{ moles yr}^{-1}$

^{a)} Methyl iodide flux calculated using historical wind speed averaged for 25 years based on Nightingale (1991).

^{b)} Rendell et al. (1994).

have also been reported in this region (Oram and Penkett, 1994).

The average methyl iodide seawater concentrations for each cruise is shown in Fig. 3, together with the sea-to-air flux calculated using both instantaneous and climatologically averaged monthly wind speeds. The two approaches to evaluating wind speeds can yield rather different monthly fluxes, though the sums of the monthly fluxes over the sampling period agree to within 10% of one another (5.6 and $5.2 \times 10^{-12} \text{ g cm}^{-2} \text{ h}^{-1}$ methyl iodide for climatologically averaged and instantaneous winds respectively). We have chosen to use fluxes based on climatological average wind speeds for subsequent calculations, to better represent average conditions.

The average fluxes of methyl iodide out of seawater and wet deposition of iodine to seawater are presented in Table 1 and converted to a flux estimate for the southern North Sea.

4. Discussion

The methyl iodide flux out of seawater shows a modest seasonality with minimum emissions in winter (Fig. 3). This seasonality is assumed to be linked to the seasonal biological cycle, though the exact nature of this linkage is unclear. Nightingale (1991) noted a correlation between monthly average methyl iodide and chlorophyll a concentrations (taken as a measure of phytoplankton biomass) in the southern North Sea ($r = 0.81$, $n = 9$). However, the seasonality of methyl iodide concentrations and emissions is much less

pronounced than that observed for dimethyl sulphide in the same region (Liss et al., 1994a), a gas with a well documented phytoplankton source (Liss et al., 1994b). Significant amounts of methyl iodide continue to be produced in winter, even though phytoplankton productivity has fallen to very low levels (Howarth et al., 1994). We suggest therefore that while the production of methyl iodide in this region is related to the seasonal cycle of primary productivity, the connection is not necessarily direct or simple.

Although the driving mechanisms regulating the emission of methyl iodide are not clear, the seasonality noted here is consistent with the seasonality in atmospheric methyl iodide concentrations over North Norfolk (Oram and Penkett, 1994) and the Oregon coast (Rasmussen et al., 1982).

Total iodine rainwater concentrations also show an apparent seasonality with lower concentrations in winter ($2.9 \pm 1.1 \text{ nM}$, $n = 11$) and higher but variable values throughout the rest of the year (8.2 ± 8.3 , $n = 29$). This variability of rainwater iodine concentrations is typical of the behaviour seen for all species with short atmospheric lifetimes, though average fluxes based on long sampling programmes such as this yield consistent values (Jickells, 1995). As with methyl iodide, winter iodine concentrations in rain do not fall to very low levels (Fig. 2). Rainfall amounts in this area show little seasonality so fluxes follow rainfall concentrations. Heaton et al. (1990) also noted a seasonality in rainwater iodine concentrations and Barrie and Barrie (1990) reported a seasonality of aerosol iodine levels in the Canadian Arctic which

they related in part to an assumed seasonality of methyl iodide production and in part to polar photochemical cycles.

Thus, it seems likely that the production of methyl iodide is seasonal over a wide area, driven in some way by marine primary production, and that this seasonality is also reflected in atmospheric concentrations of methyl iodide, aerosol iodine and ultimately iodine deposition.

The annual average total iodine concentrations in rainwater is 6.8 ± 7.5 nM ($n=40$). Average iodate and iodide concentrations are 3.1 ± 2.7 and 3.7 ± 6.6 nM respectively (excluding the extreme value for 30 September and 17–24 November, gives average iodate and iodide values of 3.0 ± 2.3 and 2.4 ± 2.0 nM, respectively). There is no evidence of seasonality in the iodide/iodate ratio. The likely initial products of the photolysis of methyl iodide in the atmosphere are HOI, HI, I_2O_2 and $IONO_2$ (Jenkin et al., 1985; Chatfield and Crutzen, 1990; Chameides and Davis, 1980). The results presented here indicate there must be further oxidation to yield iodate. Given the hinderances to chemical oxidation (Luther et al., 1995), this oxidation may also be photochemical. The lack of seasonality in the iodine speciation in rainwater implies that the redox reactions are of similar efficiency in winter and summer, albeit at lower iodine concentrations in winter.

Iodate is the only iodine species in the atmosphere which is apparently inert to photolysis (Chatfield and Crutzen, 1990). These authors have emphasised the importance of this type of redox information in constraining models of the atmospheric chemistry of iodine and its role in other oxidation reactions. Our detection of significant amounts of iodide in rainwater implies there is the potential for aerosol iodine to continue to undergo photochemical reactions.

Cutter and Church (1986) and Scudlark and Church (1988) have attempted to use the redox speciation of arsenic and selenium in rainwater to evaluate the oxidising capacity of the atmosphere. It may be that iodine redox speciation can also be used in this way, though the evident complexity of the atmospheric iodine cycle makes the interpretation of this information difficult.

The proportion of the total iodine present as iodide in these North Sea rain samples is about 50%. This is similar to the proportion of reduced selenium (IV) to total selenium (56%, Cutter

and Church, 1986) while reduced arsenic (III) constituted 0–40% of total arsenic (Scudlark and Church, 1988). In both these studies the redox ratios varied considerably between samples, though there was no obvious single factor controlling this variability. Thus, it does not yet seem possible to use these redox ratios to assess the oxidising capacity of the atmosphere.

4.1. An iodine air-sea exchange budget

In this section we attempt to construct a budget comparing methyl iodide emission and wet deposition fluxes. The fluxes are presented in Table 1. This budget considers only methyl iodide emissions, although as discussed earlier some other organo-iodine gases may be emitted from seawater. This emission estimate is therefore likely to be an underestimate. Furthermore we consider only wet deposition of iodide and iodate. We believe that methyl iodide is unlikely to be present in our rain samples after extended storage periods, and that other iodine species are unlikely to contribute significantly. Dry deposition of aerosol iodine may contribute an additional flux. Unfortunately we do not have aerosol iodine concentrations for the North Sea region. However, the available data from some disparate sampling sites from American Samoa to the Canadian Arctic (Arimoto et al., 1987; Sturges and Barrie, 1988) span a relatively narrow range of $0.5\text{--}3$ ng $I\ m^{-3}$. Assuming these figures represent a general global background level and using published deposition velocities for iodine derived from studies of radioactive iodine released during the Chernobyl incident ($0.2\ cm\ s^{-1}$ Jylha, 1991), we can make an estimate of the importance of dry deposition. These calculations suggest that the inclusion of dry deposition could increase total deposition estimates over that from wet deposition alone by 9–55% to $6.5\text{--}9.3 \times 10^5$ moles yr^{-1} .

The striking result from Table 1 is that despite the relatively limited data sets available, the two fluxes are remarkably similar. Methyl iodide emissions from seawater and iodine air-to-sea wet deposition appear to be approximately in balance on a local scale. This result is not substantially altered even if total iodine emissions are increased by 50% as a result of including other organo-iodine species (see introduction), particularly if the increase in total deposition flux arising from dry deposition is also considered.

Table 2. Total iodine concentrations in precipitation

Fuge and Johnson (1986) review	4–160 nM (data up to 1981)
Heaton et al. (1990) US east coast	17 nM (“warm” season) 11 nM (“cold” season)
Luten et al. (1978) Dutch coast	8, 13 and 28 nM
Arimoto et al. (1987) South Pacific	2.7 ± 0.9 nM (<i>n</i> = 19) Samoa 12.0 ± 2.4 nM (<i>n</i> = 14) Enewetak
Jickells et al. (1992) Scottish winter	0.6 nM (snow)
Barrie (1988) Dorset, Ontario	11–76 nM
this study	1–41 nM (<i>n</i> = 40)

Our results are all for the southern North Sea and thus we can generate emission and deposition fluxes directly for this area. However, given an atmospheric lifetime for methyl iodide of about five days (Solomons et al., 1994) it is unlikely that methyl iodide released from the southern North Sea will be oxidised, absorbed onto aerosol particles and rained out within this region. It is necessary then to consider the broader scale and it is interesting to note that methyl iodide fluxes from sea-to-air at a number of sites world wide appear to be rather similar, particularly compared to the wide variations seen in DMS fluxes (Lovelock et al., 1973; Rasmussen et al., 1982; Singh et al., 1983; Nightingale, 1991; Liss et al., 1994a, b). Rainwater iodine concentrations reported at a number of sites from around the world also fall into a relatively narrow range, even though some of these sites include continental rain (Table 2). The relative uniformity of aerosol iodine concentrations was also noted earlier.

5. Conclusions

If the approximate balance between methyl iodide flux and iodine deposition (Table 1) is not simply fortuitous, it may imply that marine biogenic emissions from large areas of the North Atlantic upwind of the UK are relatively uniform on time scales of weeks and months. This, coupled to 5-day atmospheric lifetime of methyl iodide means that average deposition fluxes are also rather uniform in space, and show similar seasonality to

that of methyl iodide. However, the extreme values of atmospheric methyl iodide noted by Oram and Penkett, 1994, and rainwater total iodine concentration (Fig. 2) indicate that this uniformity does not hold on shorter time scales.

If this suggestion of a regionally homogeneous source is realistic, it should be possible to scale our North Sea methyl iodide emissions to a global estimate. This yields a source strength of about 0.15 Mtons yr⁻¹, a figure lower than the existing estimates (Chameides and Davies, 1980; Reifenhauer and Heumann, 1992). Although the seasonality in iodine deposition is not well defined, the average winter concentration is significantly lower than for the rest of the year at the 98% confidence level. The lack of seasonality in the iodine speciation in rain seems to imply that redox reactions are of similar efficiency in winter and summer.

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