

## STSM REPORT

### Measurement of total iodine and iodine speciation in marine aerosol

*COST Action number:* 735  
*Beneficiary:* Dr Rosie Chance, Department of Chemistry, University of York, UK.  
*Host:* Dr Ben Gilfedder, Institute of Environmental Geology, Technische Universität, Braunschweig, Germany.  
*Period:* 26/4/09 to 14/5/09  
*Place:* Braunschweig, Germany.  
*Reference code:* COST-STSM-735-04685

#### Summary

Dr Chance visited the Institute of Environmental Geology, Technische Universität, Braunschweig, Germany, in order to use a new thermo-extraction spectrophotometric method developed by Dr Gilfedder for determination of particulate iodine. Following training, a set of marine aerosol samples collected in the tropical east Atlantic was analysed for total particulate iodine. The precision of the method was 5% or less and the limit of detection equivalent to 6 pmol I m<sup>-3</sup> air. Sample concentrations ranged from 16 to 97 pmol m<sup>-3</sup>, with a median value of 46 pmol m<sup>-3</sup>. Aqueous extracts of the samples were prepared and will be analysed for water soluble iodine by inductively coupled plasma mass spectrometry (ICP-MS) by Dr Gilfedder. It is anticipated that these measurements will form the basis of a publication. Total iodine and was also measured in phytoplankton material prepared from laboratory cultures. Total carbon in these samples was measured using a Euro EA Elemental Analyser, and iodine:carbon ratios calculated. Initial results suggest molar iodine:carbon ratios between  $2 \times 10^{-7}$  and  $1 \times 10^{-5}$ , which is lower than has been reported for marine particulate. Whether these low values are an accurate reflection of the iodine content of laboratory grown phytoplankton cultures or the result of unanticipated losses during sampling and measurement is currently under investigation. Ongoing collaboration with the host will develop the use of the thermo-extraction method as a means of determining iodine content of phytoplankton. Participation in the STSM has strengthened links between the research groups involved and it is anticipated that this may lead to further collaborations in the future.

## **1. Rationale and objectives**

Iodine gases are involved in ozone depletion and particle formation reactions in the marine boundary layer and may thus impact climate. Recycling of iodine from the aerosol to the gas phase is thought to be controlled by its chemical speciation within the aerosol. Total particulate iodine is usually determined by neutron activation analysis (NAA) e.g. (Baker et al., 2000), however this is expensive and few facilities exist.

The host, Dr Gilfedder, has developed a new thermo-extraction spectrophotometric method for determination of particulate iodine (Gilfedder et al., 2007). The main objective of the STSM was to use this technique to determine total iodine in a set of marine aerosol samples from the tropical east Atlantic, collected by Dr Chance during the UK-SOLAS INSPIRE cruise (RRS Discovery cruise D325). It was also hoped that water soluble iodine in the aerosol samples would be measured by inductively coupled plasma mass spectrometry (ICP-MS) and iodine speciation in this fraction determined using ion chromatography – inductively coupled plasma mass spectrometry (IC-ICP-MS).

The second objective of the STSM was to measure particulate iodine in samples of phytoplankton material from laboratory cultures, with the aim of quantifying the iodine:carbon ratio. An iodine:carbon ratio of  $1.4 \times 10^{-4}$  has been reported for Pacific phytoplankton (Elderfield and Truesdale, 1980), but no other direct measurements are available. Constraining this parameter will improve understanding of the biogeochemical cycling of iodine and its subsequent volatilisation from the ocean surface.

## **2. Description of work**

### *Week 1*

Training in the use of ICP-MS to determine water soluble iodine was undertaken. This included operation of the instrument, the use of standards, internal standards and reference materials, optimization and trouble shooting. A number of aerosol samples were extracted in preparation for analysis. Unfortunately, at this time the instrument performance was not satisfactory due to unexpected deterioration of the vacuum pump, so it was not possible to analyse the samples. A new pump was ordered immediately, but did not arrive until the final day of the STSM so no further ICP-MS work could be undertaken. It was agreed that the sample extracts will be analysed by Dr Gilfedder following installation of the new vacuum pump.

### *Week 2*

Training in the thermo-extraction spectrophotometric method for determination of particulate iodine was undertaken. This method involves the combustion of samples at 1000°C in a stream of oxygen gas. The iodine thus volatilised is trapped by bubbling through ultrapure water and quantified by a catalytic  $\text{As}^{3+}$ - $\text{Ce}^{4+}$  UV/Vis spectrophotometric method. Reference materials are analysed in every batch in order to check the recovery and reproducibility of the method. The set of aerosol samples were analysed for total particulate iodine. Replicate analyses of selected samples were made in order to estimate the precision and limit of detection of the method. An additional set of aerosol samples that has previously been analysed for iodine content by NAA were received from Dr Alex Baker at the University of East Anglia, UK.

These samples will be analysed by the thermo-extraction method as an aerosol reference material to further validate the method. However, as these samples were collected on cellulose acetate filters rather than quartz fibre filters (as the Atlantic samples were), it is necessary that a catalyst such as platinum is added to aid combustion. During the STSM, a potential platinum catalyst was analysed to evaluate its suitability.

### *Week 3*

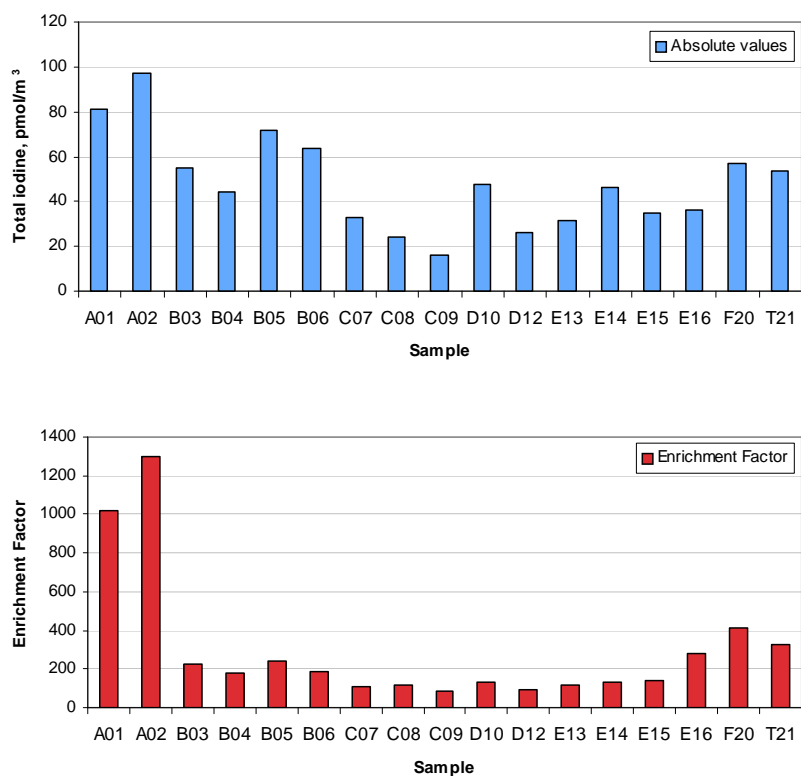
Marine phytoplankton samples prepared from laboratory cultures were analysed for total particulate iodine and total carbon. Samples of five phytoplankton strains grown under natural and elevated iodide concentrations were prepared by Dr Claire Gachon at the Scottish Association for Marine Science, UK. Samples of a further four strains of phytoplankton isolated from coastal waters on the western Antarctic Peninsula were prepared by Dr Claire Hughes at the University of East Anglia, UK. Total carbon was measured using a Euro EA Elemental Analyser. Finally, portions of the remaining aerosol filter samples were extracted into water for analysis by ICP-MS at a later date.

## **3. Results**

### *Total Iodine in marine aerosol*

Triplicate analyses of blank aerosol filters yielded a theoretical limit of detection (three times the standard deviation of the blank) of 2 to 5 ng iodine. For a total filter area of  $\sim 480 \text{ cm}^2$ , a sampling time of 24 hours and a high volume flow rate of  $1.1 \text{ m}^3 \text{ minute}^{-1}$ , this corresponds to atmospheric iodine concentrations of between 1 and 3  $\text{pmol m}^{-3}$ . The average ( $\pm$  one standard deviation) iodine concentration of five different blank aerosol filters was  $5 \pm 3 \text{ ng per } 3.8 \text{ cm}^2$ . For the above conditions this yields a slightly higher limit of detection of  $6 \text{ pmol m}^{-3}$ .

Of five aerosol samples analysed in triplicate, the relative standard deviation (RSD) ranged from 2 to 5%. The range of iodine concentrations encountered in the aerosol samples ranged from 37 to 267 ng per  $3.8 \text{ cm}^2$  of filter, with a median value of 77 and an average value of 88 ng per  $3.8 \text{ cm}^2$ . This corresponds to atmospheric concentrations ranging from 16 to 97  $\text{pmol m}^{-3}$ , with a median value of 46 and an average value of 48  $\text{pmol m}^{-3}$  (figure 1). These values are similar to total particulate iodine concentrations measured in coastal air in the southeast of England (Baker et al., 2000).

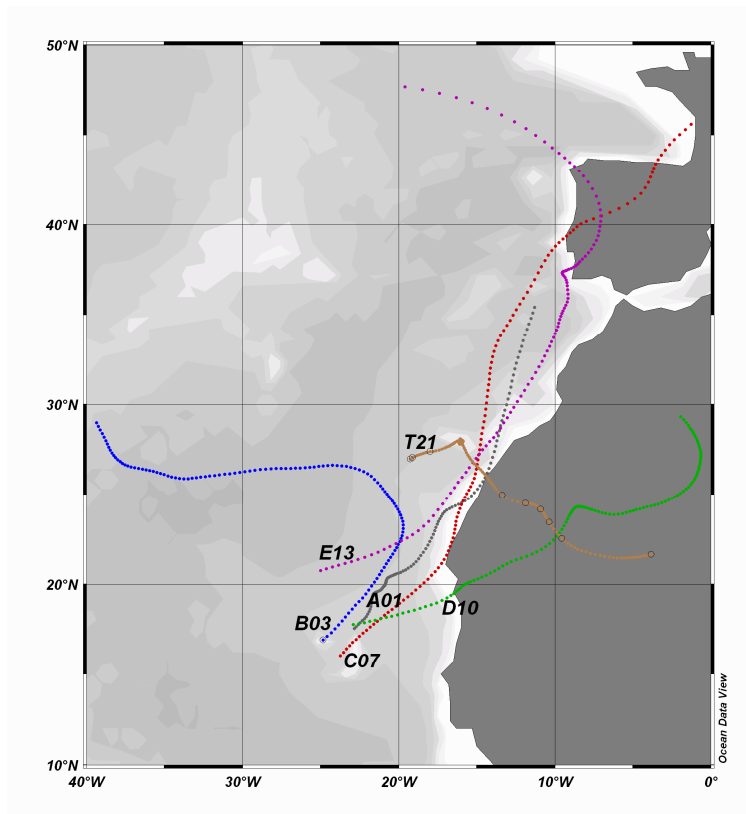


**Figure 1.** Atmospheric concentrations of total particulate iodine (top) and iodine enrichment factor (bottom) for aerosol samples collected during cruise D325 in the tropical east Atlantic.

The iodine enrichment factor (EF; figure 1) was calculated according to the relationship given in Baker et al. (2000):

$$EF = \frac{([I]/[Na])_{\text{aerosol}}}{([I]/[Na])_{\text{seawater}}}$$

Iodine was most enriched in samples A01 and A02 (figure 1), with values of 1019 and 1302 respectively. The four day back trajectory for these samples (figure 2) indicated the air sampled had travelled south along the West African coast, but was not of continental origin. It is speculated that the high iodine concentrations in these samples may have arisen from the volatilisation of iodine from either exposed macroalgae at the coast or microalgal activity in coastal waters. Iodine enrichment was lowest in samples C07 to D12, which comprised air of continental origin (figure 2). A more thorough interpretation of the results will be made using back trajectories, major ion data and other parameters such as ozone concentrations if appropriate.



**Figure 2.** Four day back trajectories showing origin of air masses arriving at each sampling station. Trajectories produced with HYSPLIT from the NOAA ARL Website (<http://www.arl.noaa.gov/ready/>), plot produced using Ocean Data View (Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2008).

Water soluble iodine had previously been measured in three of the aerosol samples and was found represent 38% of the total in each case. This is similar to the results of Baker et al. (2000), who found only ~25% of total particulate iodine was released by cold water extraction. The remaining samples have been extracted into water and will be analysed for soluble iodine by Dr Gilfedder when the ICP-MS is again operational.

#### *Preliminary iodine content of phytoplankton samples*

Iodine and carbon contents of the various phytoplankton samples analysed during the STSM are given in table 1. The calculated iodine:carbon ratios were lower than the literature value of  $\sim 10^{-4}$  (Elderfield and Truesdale, 1980) by at least an order of magnitude, and typically more than this. There are two possible reasons for this: low iodine content and high carbon content. In all cases, the iodine content of the algal samples was considerably less than reported for marine particulate collected from surface seawaters ( $\sim 50$  to  $>500$   $\mu\text{g/g}$ ; Elderfield and Truesdale, 1980; Wong et al., 1976). Whether these low values are an accurate reflection of the iodine content of laboratory grown phytoplankton cultures or the result of unanticipated losses during sampling and measurement is currently under investigation. In some cases, the carbon contents are also higher than expected for diatoms and these values are also being checked.

**Table 1.** Preliminary iodine and carbon content of phytoplankton samples and associated iodine:carbon ratios.

Algal strain	Description	I, ug/g	% C by mass	mass I/C ratio	molar I/C ratio
<i>CCAP Batch 1</i>					
1050/8	<i>Navicula</i> sp.	13.8	50	2.7E-05	2.6E-06
1050/9	<i>Navicula</i> sp.	15.8	34	4.6E-05	4.4E-06
1050/10	<i>Navicula</i> sp.	5.3	22	2.4E-05	2.2E-06
<i>CCAP Batch 2</i>					
1050/8	<i>Navicula</i> sp.	2.6	7	3.7E-05	3.5E-06
1050/9	<i>Navicula</i> sp.	1.0	42	2.5E-06	2.3E-07
1050/10	<i>Navicula</i> sp.	0.3	5	6.0E-06	5.7E-07
1055/1	<i>Phaeodactylum triconutum</i>	<LoD	3		
PAP	<i>Navicula</i> sp. (pelagic)	16.7	47	3.5E-05	3.3E-06
1085/12	<i>Thalassiosira psuedonana</i>	6.7	13	5.2E-05	4.9E-06
<i>Antarctic isolates</i>					
RaTS 35	<i>Psuedonitzschia</i> sp.	5.7	6	1.1E-04	1.1E-05
RaTS 9	Centric diatom	14.9	36	4.5E-05	4.3E-06
RaTS 28	Centric diatom	10.5	16	6.6E-05	6.3E-06
RaTS 31	<i>Psuedonitzschia</i> sp.	7.7	33	2.5E-05	2.4E-06

a. Not yet blank corrected

Analysis of the phytoplankton samples highlighted some ways in which the preparation of the filters can be improved. Reproducibility was found to be better when the volume of algal culture applied to the sample was less – where a larger sample volume had been applied to the sample, inhomogenous coating and flaking during handling led to poor reproducibility. Agreement between repeat experiments of the same culture strain (1050/8, 1050/9 and 1050/10) was also poor for both iodine and carbon content. Blank samples prepared by filtering cell-free algal growth media were found to contain unexpectedly high levels of iodine, indicating the need for a rinse step to remove any soluble iodine retained on the filter or the extracellular space. In the case of algae grown under high iodide concentration, even the media blank contained such high levels of iodine that the method response was saturated.

#### 4. Future collaboration

Throughout the STSM, extensive discussions were held between Drs Chance and Gilfedder concerning collaborative work. It was agreed that Dr Gilfedder will analyse the aqueous aerosol extracts prepared during the STSM for total water soluble iodine using ICP-MS. If sample volume allows, iodine speciation in the extracts will also be determined by IC-ICP-MS. Ongoing collaborative work will also develop the use of the thermo-extraction method as a means of determining iodine content of phytoplankton and attempt to resolve the issues with this approach described in section 3.

In the longer term, it is hoped that the complementary mass spectrometric techniques available at Braunschweig (IC-ICP-MS) and York (liquid chromatography- tandem mass spectrometry and high resolution mass spectrometry) may be jointly applied to the investigation of soluble organic iodine compounds in marine aerosol. Discussions of how this might practically take place (e.g. overcoming the different mobile phase requirements of the instruments) are ongoing. Additional possibilities of collaboration, for example in future field campaigns, was also discussed. Participation

in the STSM has helped forge strong links between the research groups involved and it is anticipated that this may lead to further collaborations in the future.

## **5. Projected Publications**

It is hoped that the work completed during this STSM will contribute to a number of scientific publications:

- A paper describing and interpreting total particulate and soluble iodine in the tropical Atlantic aerosol samples.
- A methodology paper describing the use of the thermo extraction-spectrophotometric method for the determination of particulate iodine in aerosol samples. This will include the quality control data from the aerosol samples analysed here, along with further validation using the cellulose filters provided by Dr Baker.
- A paper presenting measurements of iodine:carbon ratio in marine phytoplankton. The results collected thus far are preliminary, but it is hoped that on going collaboration will result in a publishable data set.
- The aerosol iodine results may also be presented in a poster at the International SOLAS Open Science Conference in Barcelona in November 2009.

## **References**

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