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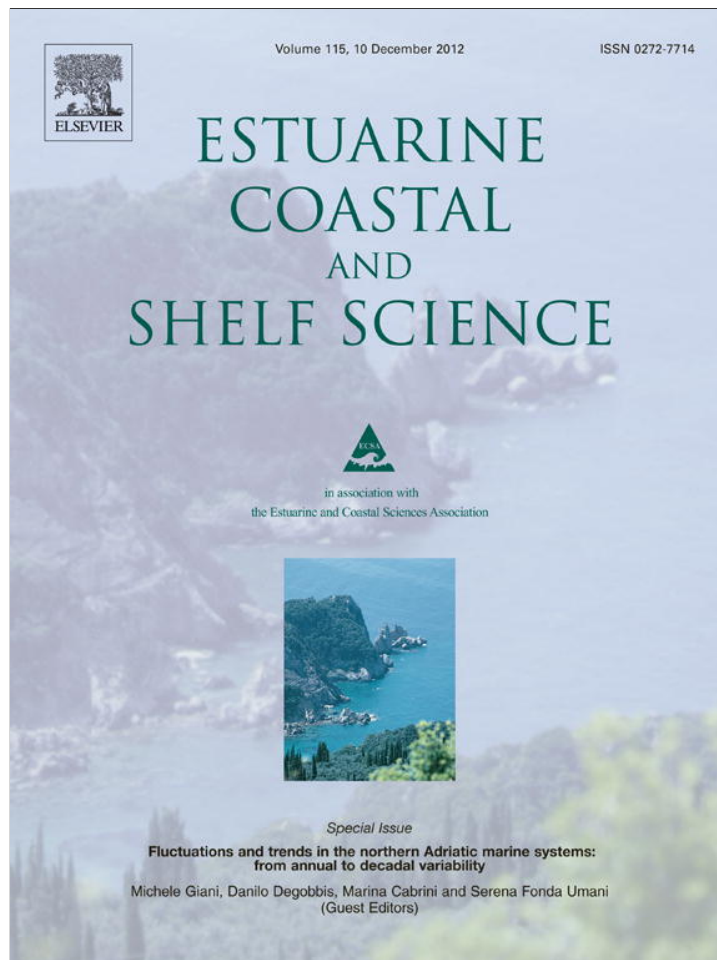
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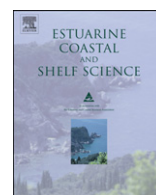
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Circumstantial evidence in support of org-I as a component of the marine aerosol arising from a study of marine foams

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ABSTRACT

A study of foams formed on the marine Lake Mir, Croatia, and elsewhere on the same coast demonstrates, for the first time, that they are fractionated (enriched) in org-I by up to 630 times relative to the water from which they form. The results are consistent with an I/C mole ratio for in-situ organic matter. Foams created artificially in the laboratory from natural samples of water from Lake Mir were similarly fractionated, although to a lesser degree. These differences were effectively removed when enrichments were expressed as molar ratios, e.g., $P_{\text{tot}}/I_{\text{tot}}$, rather than straightforward concentrations. This similarity in the behaviour to enrichment for organic forms of I, N and P suggests that the time over which foams age is a major determinant of the enrichment they display. It is argued that this period allows time for the seawater occluded in the interstitial spaces between bubbles, to drain away. Since foam production is ubiquitous over the oceans it seems likely that this process local to coastal environments is much more common than at first might appear to be the case. The paper explains how this work provides circumstantial evidence that the bubble-bursting mechanism current since the 1960s may well provide the iodine which appears to be missing in many modelling calculations based upon an atmospheric system dependant upon sorption of the species IO upon the marine aerosol.

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1. Introduction

With its large atomic size, the element iodine is represented within the natural environment by many compounds and radicals in different oxidation states. In the oceans, the largest reservoir of iodine on the Earth, iodide and iodate ($I(-1)$ and $I(+5)$ respectively) are the principal dissolved iodine species, at a total concentration of about $0.45 \mu\text{mol l}^{-1}$ (Sugawara and Terada, 1957; Truesdale, 1975; Elderfield and Truesdale, 1980; Nakayama et al., 1989; Wong, 1991; McTaggart et al., 1994; Truesdale, 1994; Campos et al., 1999). Particulate-I exists at pmol l^{-1} concentrations (Wong et al., 1976), while dissolved organically bound iodine is a minor component (Truesdale, 1975), representing only few percent of the total dissolved iodine pool. The presence of iodide is generally related to the euphotic zone; in deep-ocean waters the iodine system approaches thermodynamic equilibrium, with iodate predominating (Tsunogai

and Sase, 1969). Meanwhile, in coastal and estuarine waters of high primary productivity dissolved organically bound iodine can sometimes exceed the sum of the inorganic fractions (Luther and Campbell, 1991; Wong and Cheng, 1998, 2001; Cook et al., 2000; Schwehr and Santschi, 2003), and the same pattern applies to limnic and anchialine environments (Gilfedder et al., 2009; Žic et al., 2010). In anoxic seawater, for example, in deep unventilated basins or intermediate waters in which regenerative processes prevail, iodine is present as iodide (Wong et al., 1985; Luther and Campbell, 1991; Farrenkopf et al., 1997).

Oceans are the major source of atmospheric iodine, and consequently the most important iodine supplier to terrestrial environments. Within the atmosphere, iodine occurs typically at concentrations of about $10\text{--}100 \text{ ng m}^{-3}$, within a photochemical system rich in species. In modelling the atmospheric iodine system Saiz-Lopez et al. (2012) list approximately twelve gaseous species which cover oxidation states -1 to $+5$ with, for example, I^- and HI representing $I(-1)$, I_2 representing $I(0)$, and HIO, IO, I_2O_3 , I_2O_4 , and I_2O_5 representing oxidation states between $I(+1)$ to $I(+5)$. Carpenter (2003) used 9 species, including INO_2 , IONO_2 , I_2O_2 , IO_2 . Some additional, iodo-alkanes, representative of a reduced state, were included in both models. Whatever the precise listing is of the

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gaseous species, in both models they are assumed to sorb to the atmospheric aerosol. This aerosol is fundamental to cloud seeding which, in turn, is important in both climate control through its effect upon the Earth's albedo, and in the biogeochemical cycling of the major ions contained in rain. It can be seen from these two choices of candidate compounds that there has been, and possibly still is, considerable improvement to be made in the basic design of atmospheric iodine models. The results of such modelling, which is a considerable achievement in itself, is that the central role of the IO species is compromised by the lack of a supply flux – there is insufficient iodine within the model to sustain it (Jones et al., 2010). Org-I in the marine aerosol is represented in the preceding models by soluble organic iodine (SOI) which is assumed to be synthesised from the reaction of the gaseous iodine species with the aerosol organic matter (Gilfedder et al., 2008). No direct incorporation of organically bound iodine from the sea surface during bubble bursting (Seto and Duce, 1972), is countenanced.

Since about the early 1960s much attention has been given to the marine aerosol and it was established that some elements (e.g., N, P, I, and transition metals) are fractionated during its production from seawater. For example, in the case of iodine, fractionation relative to chlorine, $F(I)_{Cl}$, was detected as variation from 1, of the ratio of the concentrations of iodine and chlorine (or sodium) in the aerosol, as compared with that in the seawater from which the aerosol arose:

$$F(I)_{Cl} = \frac{\left(\frac{[I]}{[Cl]}\right)_{atm}}{\left(\frac{[I]}{[Cl]}\right)_{sw}} \quad (1)$$

where, $F(I)_{Cl}$ was ~ 50 – 1000 (see: MacIntyre, 1974). Explanations for this were sought under the initial assumption that the major ions of seawater (Cl^- and Na^+) were not themselves fractionated. Although the position on that has softened slightly (MacIntyre, 1974), in the case of iodine fractionation the situation remains essentially the same because the fractionation for iodine is so high. This led to the idea that I_2 might 'evaporate' from seawater under the influence of UV-light (Miyake and Tsunogai, 1963; Martens and Harriss, 1970), and subsequently attach itself to the aerosol. At the same time though, it was found that UV-light could increase the mobility of iodine within the aerosol, itself, leading to a secondary type of fractionation. The advent of the electron-capture detector enabled Lovelock et al. (1973) to discover that a flux of iodo-methane from phytoplankton is emitted from the sea-surface. This area has since expanded greatly, and a range of org-I compounds have been detected in the marine boundary layer, for example, CH_3I , C_2H_5I , CH_2I_2 , CH_2I_2 , CH_2I_2 , CH_2I_2 , CH_2I_2 , CH_2I_2 (see Saiz-Lopez et al., 2012 for a detailed review). Such experimental evidence seems to have allowed the iodoalkane mechanism to overtake that for an I_2 flux. Interestingly though, it seems also to have obscured the experimental evidence that higher molecular weight org-I might be incorporated into the aerosol at the early, bubble-bursting stage.

The presence of relatively high molecular weight org-I in the matrix of the aerosol was predicted by the bubble-bursting mechanism, whereby organic matter in the marine micro-layer becomes highly fractionated during the formation of 1–5 jet-droplets when a bubble bursts at the sea-surface. These droplets form when the tension in the lower hemisphere of a bubble is suddenly relaxed by the bubble's bursting. The significance of the Seto and Duce (1972) experiment is that it provided experimental evidence for the fractionation of this kind of org-I during aerosol formation, and showed that there was no corresponding evidence for inorganic iodine fractionation. In this inspired experiment, they grew the alga *Phaeodactylum tricornutum* in a culture laced with $^{131}I^-$, and

extracted the labelled organically bound iodine. The extract could reasonably be expected to contain compounds of larger molecular weight, such as di-iodo-tyrosine which is known to have biological functions (see: Hou et al., 1997; Truesdale, 2008). It was then added to the artificial ocean from which their aerosol would be generated, where it enhanced the iodine content of the aerosol considerably. Incidentally, this whole story of the fractionation of iodine during aerosol production has a counter-point in the Chapman and Liss (1981) finding that inorganic forms of iodine in seawater are not enriched to a significant extent in the oceanic surface micro-layer. With the micro-layer being an antecedent of the jet-droplets, this negative result actually supports the work of Seto and Duce (1972).

The explanation for I_2 has continued and it is now known to be released into the atmosphere in the littoral zone by some large seaweeds (Palmer et al., 2005; Küpper et al., 2008), where it can participate in the atmospheric photochemical system, as already outlined. It was previously suspected that I_2 might also play a major role in the oxidation of iodide to iodate in seawater since, at the alkaline pH of seawater, it should spontaneously disproportionate to iodate and iodide (Sugawara and Terada, 1958). However, the discovery that I_2 reacts very rapidly with substances dissolved in seawater, probably organic matter (Truesdale, 1974; Truesdale et al., 1995, 2003), now makes this kinetically less tenable. Incidentally, it is important to understand that if I_2 is added to seawater, within seconds it will hydrolyse to give an equilibrium system involving I_2OH^- , HOI , OI^- , I^- , and some ICl (Truesdale et al., 2003), and it could be any one or more of these oxidised forms which actually reacts with organic matter. To the extent that I_2 actually occurs transiently in seawater then, these other compounds must also occur naturally. It must be recognised though that this group of compounds is at very much lower concentrations than the iodate and iodide which predominate in seawater. More recently, it has also been confirmed that the predominant iodine species of seawater are unlikely to produce I_2 themselves through a direct photochemical reaction in surface water (Truesdale, 2007).

Murphy et al. (1997), using laser ionisation spectrometry at Cape Grim, Tasmania, report the presence of two iodine enrichments within the aerosol: a moderate one in many particles and a few I-rich particles. They identify a correlation between iodine and organics as clearly consistent with org-I, but that it does not preclude deposition of iodine from the gas phase. At the same site, but with different instrumentation, Middlebrook et al. (1998) detected internal mixtures of sea-salt compounds and organic species in over half of their spectra for clean marine air masses. The aerosol organics appeared to have two distinct source mechanisms, dependent upon the aerosol age. The least type of particle contained organics and sea salt, but with very little sodium sulphate. They attributed these to marine particle formation in the marine boundary layer through bubble bursting – new aerosol. This left the majority of particles, as aged particles which had absorbed various iodine gases from the photochemically maintained atmospheric system. O'Dowd et al. (2004), seem to be the first to show that biogenically driven organic contribution to marine aerosol is substantial, and they considered that bubble-bursting might be the key supplier. Baker (2005) discussed the importance of Soluble Organic iodine but does not appear to involve any insoluble component. Later, Jones et al. (2010) concluded that the combined fluxes of volatile organic iodine compounds emanating from the sea would support only ~ 10 – 25% of the observed IO levels in the atmosphere in the tropical east Atlantic Ocean around Cape Verde. Once again, they remark that a substantial additional source of iodine was needed. In a throw-back to earlier work, Saiz-Lopez et al. (2012) mention that Tsukada et al. (1987) appeared to be the first to measure the insoluble of iodine in the aerosol.

The work within this paper arose out of an iodine survey conducted on the Croatian marine lake, Mir in 2010, details of which are described elsewhere (Žic et al., 2012). The lake was chosen after Žic and Branica (2006) and Žic et al. (2010) had shown that another, physically comparable Croatian anchialine system (Greek: $\alpha\gamma\chi\iota\text{-}\acute{\alpha}\lambda\acute{\omicron}\sigma$ – near the sea; Holthuis, 1973) acts as isolated “reactor” in which various biogeochemical processes, including those of iodine, manifest themselves differently to that in the open sea. Our interest in Mir was justified because, in spite of its nearness to the surrounding Adriatic (≈ 90 m) it displayed, for example, a four times lower concentration of total iodine than the near-by open seawater, with insignificant concentrations of iodate ($\approx 0.02 \mu\text{mol l}^{-1}$). Of immediate interest here though, is that due to a strong south wind in September 2010 our attention was drawn to dense foam on the lake’s surface and around its periphery. As we were unaware of any analysis of iodine in such material we undertook a serendipitous, preliminary investigation to establish whether foam is implicated in iodine cycling in the lake. Subsequent laboratory analysis has shown the total iodine and the org-I in the foam to be enriched by 460–630 times, relative to the surface water in the lake. This paper describes all of our foam analyses, including natural foams from Lake Mir and some other Croatian waters, and laboratory-foams generated from Lake Mir samples. The paper then goes on to relate our observations to the current literature on the sea-air transport of iodine. Their significance is that they provide additional circumstantial evidence that org-I will fractionate into the sea-surface micro-layer and thereby become available as a supply-flux of iodine to the marine aerosol.

2. Study area

Lake Mir is a marine lake located at the eastern coast of the Adriatic Sea ($43^{\circ}53'12''\text{N}$, $15^{\circ}10'\text{E}$), at the south-eastern part of the island of Dugi Otok in the Nature Park Telašćica (Fig. 1), formed by marine submersion of karst uvala (compound sinkholes). The lake is elongated, $\approx (0.9 \cdot 0.3)$ km, with a surface area of $\approx 0.23 \text{ km}^2$ and a maximum depth of around 7 m. The nutrient concentrations in the lake are elevated, and the phytoplankton abundance and

biomass are comparable to those from productive Adriatic and Mediterranean coastal areas (Carić et al., 2010). Two other incidental sampling sites were used. Firstly, Velike Soline which is a shallow marine lake (up to 1 m) situated at middle-part of the eastern coast of the Adriatic Sea ($43^{\circ}42'45.32''\text{N}$, $15^{\circ}52'36.26''\text{E}$) (Fig. 1). This second lake is connected directly to the nearby Adriatic through a narrow (<4 m) and shallow (<2 m), 1 km-long channel. In the period between December and May the lake is euhaline and mesotrophic, while between June and November it becomes hypersaline ($S \approx 70$) and eutrophic (Carić et al., 2011). Secondly, the estuary of the karstic, Krka river ($43^{\circ}43'9.71''\text{N}$, $15^{\circ}51'36.18''$) (Fig. 1) is highly stratified, and, from a hydrochemical perspective, the nutrient regime results from the interaction between the nutrient rich freshwater and oligotrophic seawater (Cetinić et al., 2006).

3. Sampling, storage, foam generation and analysis

3.1. Sampling and storage

Natural foams were collected at three different locations, viz. Lake Mir, Krka Estuary and Velike Soline (Fig. 2a, b and c, respectively), on each of two occasions (Table 2). Unfortunately, no significant foaming was observed on the open Adriatic Sea station during any of the visits over the summer 2011. (Nevertheless, natural foam was observed both in the lake and the surrounding Adriatic during a visit in April 2012, although this was outside the period available for analysis. The foam on the Adriatic appeared to be in windrows.) Natural, unfiltered water samples for foam production were taken at Lake Mir between June and September 2011, as well as at nearby Adriatic station.

Natural and laboratory generated foam samples were left standing to liquefy spontaneously, and the solution was decanted either into LPDE 30 ml Nalgene bottles for iodine and nutrient analyses, or into 24-ml glass tubes equipped with a teflon/silicone septum (Wheaton) for total organic carbon analyses. These samples were diluted with Milli-Q water prior to analyses, to obtain concentration ranges optimal to each analytical method. Surface water samples from Lake Mir were collected on each occasion when either natural foam was collected, or laboratory foams were generated (Table 2). All water samples were stored in the dark, at 4°C . Nutrients were analysed within 48 h, iodine speciation within on week, while samples for total organic carbon were poisoned with NaN_3 (Aldrich).

3.2. Foam generation

Laboratory foam samples were produced by blowing air through a glass frit immersed in 0.90–0.95 l of unfiltered water sample placed in a 1 l Büchner flask (Fig. 2d). This gave a head space below the side arm of about 40–50 mm. After an initial slow increase in air-flow over about the first minute the pump (Tetratec® APS Air Pump, model APS 300) supplied about 2.5 l min^{-1} for an additional 10 min. Generally though, no foam reached the flask outlet after 5–7 min so to receive sufficient volume of foam for the replicate analyses, a composite foam sample was collected by repeating this procedure two or three times, and on the four occasions. Unlike with lake samples, the attempts to produce foam from the Adriatic seawater were unsatisfactory, since the foam was insufficiently stable to reach the outlet.

3.3. Iodine analysis

The concentrations of iodate, iodide and total iodine in both the water samples and liquefied foams were measured by

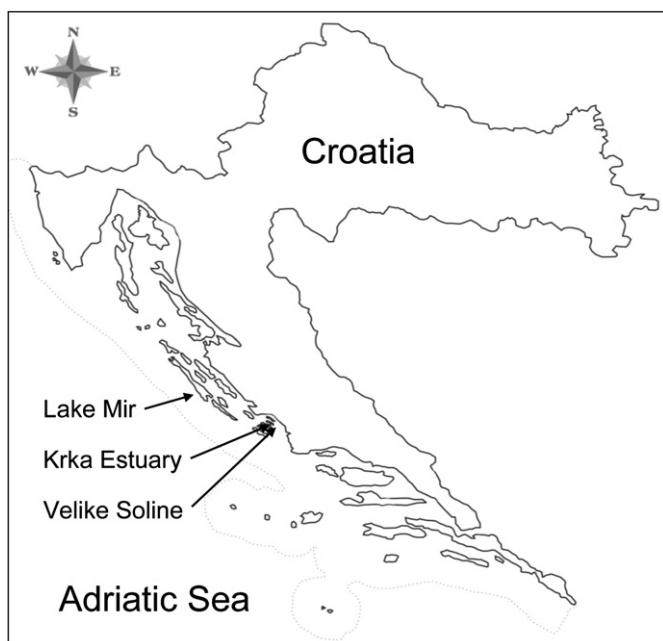


Fig. 1. The geography of the sampling locations; Lake Mir, Krka Estuary and Velike Soline.

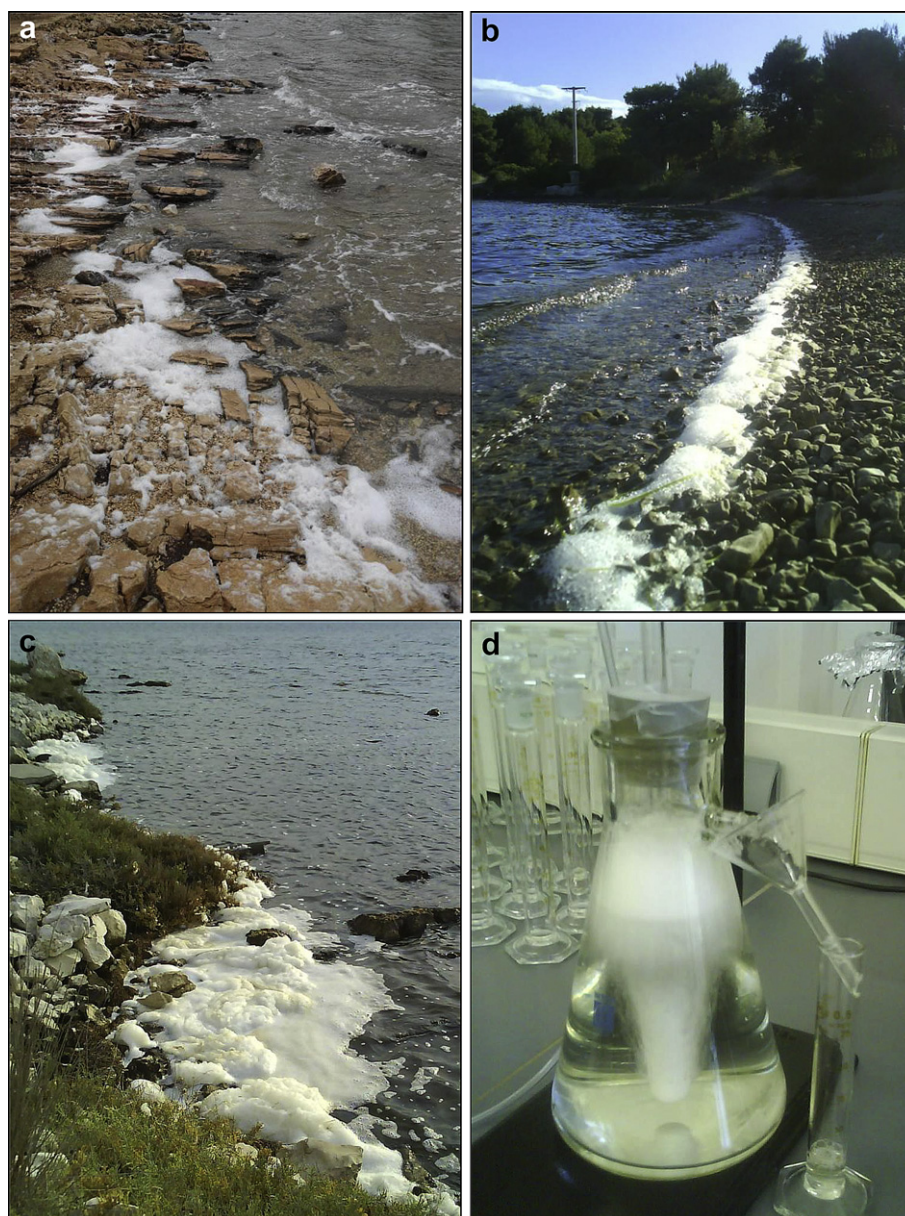


Fig. 2. Foams. Natural ones observed in (a) Lake Mir, (b) the Krka Estuary, and (c) Velike Soline. Meanwhile, (d) laboratory generation of foam in a Lake Mir sample.

voltammetry, using a PAR 384B Electrochemical Analyser in conjunction with PAR 303A static mercury drop electrode (SMDE), with a Ag/AgCl (sat. NaCl) reference electrode and a platinum wire as a counter electrode. Iodate and iodide were determined directly by differential pulse voltammetry (Herring and Liss, 1974) and cathodic stripping square wave voltammetry (Luther et al., 1988), respectively. Total iodine (TI) was determined indirectly, as iodate, after oxidation of reduced iodine species by UV-irradiation (24 h, 150-W mercury lamp; Hanau, Germany) in the presence of hydrogen peroxide. This was followed by treatment with

hypochlorite to destroy any trace of peroxide as well as to re-oxidise iodine species of lower oxidation state than iodate that might have formed during irradiation (Truesdale, 1975; Butler and Smith, 1980; Stipanicev and Branica, 1996; Wong and Cheng, 1998). To facilitate the removal of dissolved oxygen, as well as to destroy the excess of hypochlorite, sodium sulfite was also added to the samples (Wong and Zhang, 1992).

Peak currents were determined from the baseline-corrected voltammograms, with either the baseline being constructed using a spline function or by second-derivative mode implemented in

Table 1

Concentrations of total iodine, iodate, iodide, organic iodine, total phosphorus, orthophosphate and organic phosphorus (in $\mu\text{mol l}^{-1}$), and the ratios between phosphorus and iodine in surface water samples of LM – Lake Mir, Est – Krka river estuary mouth, VS – Velike Soline.

Station/date	TI (\pm sd)	Iodate (\pm sd)	Iodide (\pm sd)	Org-I (\pm sd)	P _{tot} (\pm sd)	Ortho-P (\pm sd)	Org-P (\pm sd)	P _{tot} /TI (\pm sd)	Org-P/Org-I (\pm sd)
LM 9/8/2010	0.106 (\pm 0.003)	<0.015	0.031 (\pm 0.001)	0.075 (\pm 0.003)	0.55 (\pm 0.02)	0.05 (\pm 0.00)	0.50 (\pm 0.02)	5.2 (\pm 0.2)	6.7 (\pm 0.4)
LM 10/26/2011	0.16 (\pm 0.01)	<0.015	0.032 (\pm 0.002)	0.13 (\pm 0.01)	0.65 (\pm 0.03)	0.053 (\pm 0.005)	0.60 (\pm 0.03)	4.1 (\pm 0.3)	4.7 (\pm 0.4)
Est 6/29/2011	0.339 (\pm 0.001)	0.197 (\pm 0.006)	0.094 (\pm 0.005)	0.048 (\pm 0.008)	0.40 (\pm 0.06)	<0.04	0.40 (\pm 0.06)	1.2 (\pm 0.2)	8 (\pm 2)
VS 7/28/2011	0.750 (\pm 0.005)	0.067 (\pm 0.003)	0.59 (\pm 0.03)	0.09 (\pm 0.03)	0.69 (\pm 0.01)	0.04 (\pm 0.01)	0.65 (\pm 0.01)	0.9 (\pm 0.1)	7 (\pm 2)

Table 2
Concentrations of total iodine, total phosphorus, Kjeldahl nitrogen (in $\mu\text{mol l}^{-1}$) and total organic carbon (in mmol l^{-1}) and the ratios between Kjeldahl nitrogen, total phosphorus and total iodine in natural and laboratory generated foams. LM – Lake Mir, Est – Krka river estuary mouth, VS – Velike Soline.

Station/date	TI ($\pm\text{sd}$)	P _{tot} ($\pm\text{sd}$)	N _{Kjel} ($\pm\text{sd}$)	TOC ($\pm\text{sd}$)	N _{Kjel} /P _{tot} ($\pm\text{sd}$)	P _{tot} /TI ($\pm\text{sd}$)
Natural foams						
LM 9/8/2010	48 (± 1)	220 (± 10)	8300 (± 600)		38 (± 4)	4.6 (± 0.3)
LM 10/26/2011	4.1 (± 0.4)	23.2 (± 0.3)	1150 (± 60)	11.6 (± 0.9)	50 (± 3)	5.7 (± 0.5)
Est 6/29/2011	41.3 (± 0.2)	110 (± 6)	5500 (± 700)	140 (± 5)	48 (± 6)	2.8 (± 0.1)
Est 9/13/2011	18.4 (± 0.1)	106 (± 2)	5643 (± 5)	41 (± 2)	53 (± 1)	5.8 (± 0.1)
VS 7/28/2011	5.75 (± 0.01)	19.0 (± 0.2)	930 (± 10)		49 (± 1)	3.3 (± 0.1)
VS 9/18/2011	20.4 (± 0.2)	119 (± 2)	5500 (± 40)	55 (± 3)	46 (± 1)	5.8 (± 0.1)
Laboratory foams						
LM 6/21/2011	5.9 (± 0.4)	22 (± 1)	430 (± 40)		20 (± 2)	3.8 (± 0.3)
LM 7/15/2011	4.1 (± 0.9)	8.7 (± 0.9)	320 (± 70)	4.0 (± 0.3)	37 (± 9)	2.1 (± 0.5)
LM 7/28/2011	2.2 (± 0.1)	12.4 (± 0.1)	588 (± 2)		47 (± 1)	5.7 (± 0.4)
LM 8/29/2011	1.45 (± 0.02)	8.4 (± 0.3)	340 (± 6)	6.4 (± 0.3)	40 (± 2)	5.8 (± 0.2)
LM 9/13/2011	1.16 (± 0.04)	5.7 (± 0.3)	269 (± 0.2)	5.1 (± 0.2)	47 (± 2)	5.0 (± 0.3)
LM 9/28/2011	1.2 (± 0.1)	4.8 (± 0.2)	324 (± 4)		68 (± 3)	4.1 (± 0.3)

a home-written software package, ECDSOFT (Omanović and Branica, 1998; Pižeta et al., 1999; Omanović, 2006). Calibration was by the standard addition method, and linear regression analysis was used to calculate the concentration in the original sample. This offered a high level of analytical quality control as any deterioration of the methods was detectable early, either in poor replication of the calibrations or poor overall reproducibility. Detection limits in iodate and iodide analyses were ca. $0.015 \mu\text{mol l}^{-1}$ and $0.001 \mu\text{mol l}^{-1}$, respectively. The overall precision was evaluated from sets of duplicate measurements (Currie and Svehla, 1994), and, when expressed as relative standard deviation, was typically better than $\pm 5\%$. The concentration of organic iodine was calculated as the difference between total iodine (TI) and total inorganic iodine (TII; iodate + iodide) concentration, so that precision was about $\pm 10\%$.

3.4. Nutrient analysis

The concentrations of nutrients were measured on Perkin Elmer Lambda 25 UV/Vis spectrometer. Due to the relatively high concentration of organic matter in both water and foam samples, the spectral curves were corrected for the background absorbances either by omission of a key colour-forming reagent specified by the method or by application of second derivative spectroscopy. Precision was typically better than $\pm 10\%$.

Nitrate + nitrite, nitrite and ammonium on a foam sample were measured according to Zhang and Fischer (2006), Griess–Ilosvay method (Strickland and Parsons, 1968) and ISO 7150/1:1984(E). The ISO method is based on spectrometric measurement of a compound formed by reaction of ammonium with salicylate and hypochlorite ions in the presence of sodium nitrosopentacyanoferrate (III) at about 655 nm. Kjeldahl-nitrogen (N_{Kjel}), which represents the content of trivalent negative nitrogen in organic compounds and ammoniacal nitrogen after mineralisation with selenium, was measured as ammonium (ISO 7150/1:1984(E)). The difference between the Kjeldahl- and ammoniacal-nitrogen therefore represents the organic-N fraction.

Total phosphorus concentration in water and foam samples was analysed according to ISO 6878:1998(E). The method is based on a vigorous sample mineralisation with sulphuric and nitric acids, followed by formation of phosphomolybdate complex, which is subsequently reduced with ascorbic acid to form a strongly coloured blue molybdenum complex, the absorbance of which is measured spectrometrically at about 880 nm.

In the water samples orthophosphate was measured according to the method described above, but without digestion.

3.5. Total organic carbon

To determine the total organic carbon content, an aliquot was filtered on 25-mm glass filters (GFF, Whatman) using an all-glass filtering system (Wheaton) under vacuum. All the glass equipment (filter, tubes, filtering system) was calcined at $450 \text{ }^\circ\text{C}$ for 4 h prior to use. Filters were dried to constant weight at $60 \text{ }^\circ\text{C}$, and then exposed to HCl fumes for 4 h to remove all the inorganic carbon (Lorrain et al., 2003). The dissolved organic carbon (DOC) concentrations were determined using a Shimadzu TOC-VCSH analyser, using the high-temperature ($680 \text{ }^\circ\text{C}$) catalytic oxidation method with IR detection of CO_2 (Benner and Strom, 1993), calibrated using potassium hydrogen phthalate (Fisher Scientific, Analytical Reagent grade) (Louis et al., 2009). The particulate organic carbon (POC) concentration on the filters was determined using the same equipment, via the Shimadzu SSM-5000 module which uses catalytic oxidation at $950 \text{ }^\circ\text{C}$, and is calibrated using glucose (Fisher Scientific, Analytical Reagent grade). The sum of the DOC and the POC yielded the total organic carbon content to an accuracy of 10%. Precision was typically better than $\pm 10\%$.

4. Results

The results describe a preliminary chemical investigation of natural and laboratory-generated foams, derived from Lake Mir and other marine waters. They cover the behaviour of nitrogen and phosphorus compounds as well as those of iodine and total organic-C. The reader is reminded that a statement such as, 'the concentration of iodine in the foam', actually means, 'the concentration of iodine in the liquefied foam'; with liquefied just meaning the liquid which spontaneously settled out after several hours of standing. Moreover, actual analysis was performed on a diluted sample of this liquid (see methods section).

4.1. A note on the term 'Fractionation' used here and elsewhere

The term, Fractionation, used here is essentially the same as that defined by earlier aerosol workers (see: Duce et al., 1972; MacIntyre, 1974) even though our measurements were not deliberately made relative to the major ions of seawater, e.g., Na^+ and Cl^- . Instead, our measurements refer to the ratio of the concentration of an element (either N, P or I) in foam, to that in the original seawater from which the foam was obtained. Thus, Fractionation of iodine relative to chlorine, $F(I)_{\text{Cl}}$, as defined above (Eq. (1)), can be re-written:

$$F(I)_{Cl} = \frac{\left(\frac{[I]}{[Cl]}\right)_{atm}}{\left(\frac{[I]}{[Cl]}\right)_{sw}} = \frac{\left(\frac{[I]_{atm}}{[Cl]_{sw}}\right)}{\left(\frac{[Cl]_{atm}}{[Cl]_{sw}}\right)} \quad (2)$$

In a marine system, the denominator of the re-written form is ≈ 1 because in spite of any small degree of chlorine fractionation that might have occurred, the liquid formed from the foam is still essentially seawater. Chloride analysis of one natural, and one laboratory-produced foam sample of this investigation revealed only a slight difference of <5%.

4.2. The composition of the natural and artificial foams – the raw results

The first attempt at a comprehensive analysis of the natural foam from Lake Mir was made in September 2010 and revealed a predominant organic fraction for both iodine and nitrogen. Inorganic iodine comprised only about 3% of the total iodine. With nitrogen, the organic fraction represented 78% of the total, while ammonium accounted for 18%; the rest was mainly nitrate with little nitrite. Meanwhile, organic phosphorus was the only phosphorus fraction in the foam sample, possibly also due to its prevalence in the surface water (Table 1). Because of the poor reproducibility encountered with orthophosphate determination, due to high background absorbances as well as the apparent prevalence of organic fractions, the analyses that followed were primarily to determine the total concentrations of iodine, phosphorus and reduced nitrogen, where a pre-irradiation or digestion was included.

Table 2 lists the concentrations of total iodine, total phosphorus, Kjeldahl-nitrogen and total organic carbon in 6 samples of natural foams, taken at the three sites (Fig. 1) of Lake Mir, the Krka river estuary and Velike Soline, at various times throughout the year. The raw results suggest a high degree of natural variability. Moreover, since the differences in iodine and phosphorus speciation in the water phases of these three environments is less pronounced (Table 1), the variability is probably determined by hidden variability, such as foam lifetime, which could have far exceeded the analytical uncertainty. Furthermore, a parallel investigation of foams generated artificially in the laboratory from six natural water samples taken from Lake Mir (Fig. 1, Table 2), yielded total concentrations which were much lower than those found in the natural foams, and apparently less variable. Relative to the water phase from which they were derived, iodine and phosphorus had both become fractionated in the making of the natural and artificially generated foams from Lake Mir (Fig. 3). However, whereas in laboratory generated foams total iodine and total phosphorus were fractionated by up to 40 and 47 times, respectively, the same fractionation for the natural foam in Lake Mir in September 2010 were both about an order of magnitude higher.

4.3. On the use of elemental ratios

It seemed likely that the large variations in the concentrations of the species (Table 2) would depend to an extent upon the amount the artificial foams were diluted with bulk water carried over into the collector vessel (Fig. 2d). Furthermore, that this would have a counterpart for the natural foams listed in Table 2 in respect of their age, but of which no knowledge would be available; contaminating natural water could be expected to have drained away from a long-standing foam. It was therefore foreseen that such randomness would be circumvented by the use of the element-ratios or plots of the concentration of one element against that of another in

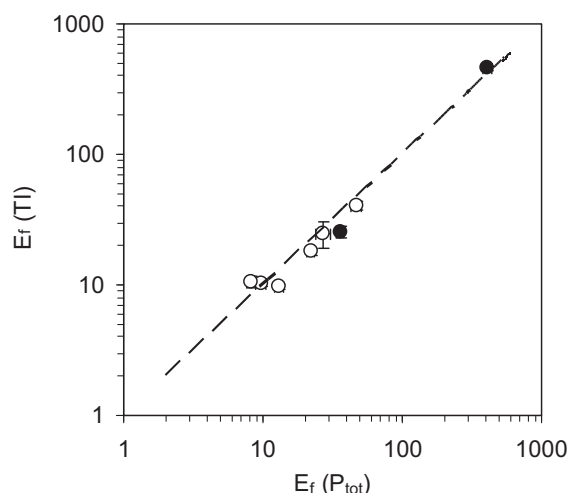


Fig. 3. A comparison of iodine and phosphorus enrichments, E_f , observed with two natural foams (black circles) and six foams generated in the laboratory from natural samples of Lake Mir water (white circles). (E_f = concentration in foam/concentration in water). Each point is an average of two runs, with each run involving separate analyses on both foam and water. Long-dashed line represents the diagonal (1:1). Note the log-scales. Error bars are mainly within the size of the symbol.

the same sample. Hence, the ratios between either N_{Kjel} and P_{tot} , or P_{tot} and TI reveal a much greater similarity in composition between natural and laboratory foams, and between laboratory foams and the water they were derived from, than do the raw results. For example, the mean P_{tot}/TI ratio of $4.7 (\pm 1.4)$ for the six natural foams is very close to that of $4.4 (\pm 1.4)$ from the six laboratory foams (Table 2), which in turn is comparable to the mean ratio of $4.2 (\pm 1.1)$ for the water phases from which the foams were generated (data not presented). These findings were confirmed statistically for each ratio ($p = 0.05$) after the differences between the means were t-tested against the standard deviation for the distribution of differences between means, with equal standard deviations. This also applied to the N_{Kjel}/P_{tot} ratios for artificial and natural foams when unequal variances were allowed for (Miller and Miller, 1988).

4.4. The change in iodine species concentration in the water during foam generation

The analyses of six Lake Mir water samples for iodide and total iodine both pre- and post the aeration (Table 3), confirmed that the aeration principally affected org-I concentrations. Note that as no iodate was detected in the samples, changes only involved either iodide or org-I concentrations. A paired t-test ($p = 0.05$) confirmed that while the iodide concentration had not changed significantly, the opposite occurred for the total iodine concentration. Hence, the average decrease in org-I concentration in the bulk water (\pm s.d.) was $28 (\pm 8)\%$. This draws a parallel with the good linear plot

Table 3
Concentrations of iodide and total iodine (in $\mu\text{mol l}^{-1}$) in natural water samples from Lake Mir before (*Ini.*) and after (*Fin.*) generation of laboratory foams.

Date	Iodide (\pm sd) – <i>Ini.</i>	Iodide (\pm sd) – <i>Fin.</i>	TI (\pm sd) – <i>Ini.</i>	TI (\pm sd) – <i>Fin.</i>
6/21/2011	0.068 (± 0.001)	0.066 (± 0.001)	0.146 (± 0.001)	0.129 (± 0.004)
7/15/2011	0.062 (± 0.003)	0.063 (± 0.001)	0.134 (± 0.002)	0.107 (± 0.001)
7/28/2011	0.066 (± 0.003)	0.059 (± 0.005)	0.166 (± 0.001)	0.135 (± 0.004)
8/29/2011	0.066 (± 0.008)	0.068 (± 0.003)	0.150 (± 0.005)	0.124 (± 0.002)
9/13/2011	0.034 (± 0.001)	0.034 (± 0.001)	0.112 (± 0.006)	0.087 (± 0.001)
9/28/2011	0.030 (± 0.001)	0.031 (± 0.001)	0.109 (± 0.006)	0.093 (± 0.007)

($r^2 = 0.968$, $n = 7$) for total iodine against total organic carbon obtained for the combined set of foam data (natural and laboratory), with the gradient (with s.e.) of $(2.9 \pm 0.2) \cdot 10^{-4}$ ($p < 0.001$) (Fig. 4).

5. Discussion

5.1. The novelty and significance of the results, overall

The results seem to present the first measurements to be made of the organic-I content of marine foam. According to our best knowledge, only Tiffany et al. (1969) reported upon iodine enrichment in a foam sample, but from the freshwater environment. Since foam is derived from the surface micro-layer (MacIntyre, 1974; Schilling and Zessner, 2011), in some way it must reflect the properties of that surface. Therefore, it is reasonable to suspect that it will also be reflected in the properties of the aerosols formed from it. It is easy to understand why such analyses were not performed before. Given Seto and Duce's (1972) inspired experiment it might well have been taken for granted that org-I compounds must exist in the aerosol. This may well have seemed to be a foregone conclusion because, in the first place, organic matter has to be present to supply the surfactants necessary for a marine micro-layer and hence, the bubbles (MacIntyre, 1974; Schilling and Zessner, 2011). Also, the complexity of the analysis of foams (or micro-layer) for org-I, especially at low concentrations, might well have dissuaded many from further study. This would agree with the fact that it has generally only been applied to the water column of near-shore environments where concentrations are relatively high (Luther et al., 1991; Stipanicev and Branica, 1996; Wong and Cheng, 1998, 2001). Even so, over the last decade more sophisticated analytical methods based upon IC-ICP-MS (Gilfedder et al., 2007), HPLC (Schwehr and Santschi, 2003) and Neutron Activation (Hou et al., 1999) have been introduced. Whatever the impediment, it has been circumvented by our serendipitous interest in the foam upon the Croatian marine lake, Mir.

Overall, the results show convincingly that, relative to the seawater from which they were derived, org-I was majorly fractionated (up to 630 times) during the production of both natural and laboratory-generated foams from lake Mir, and the other marine waters. Moreover and significantly, this did not extend to

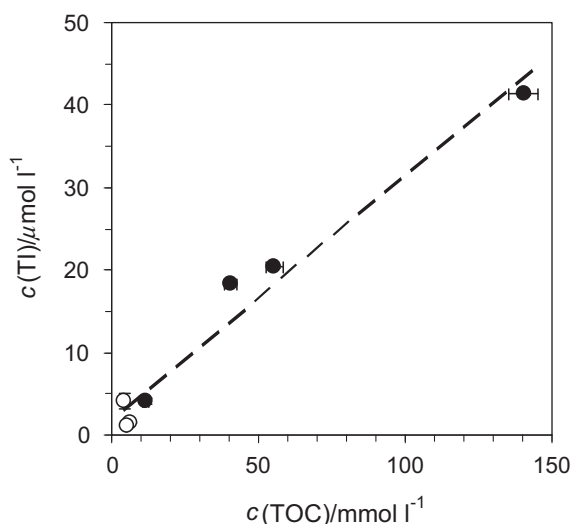


Fig. 4. The co-variation between total iodine and total organic carbon for a combined set of foam data (natural foams (black circles) from three different environments and foams generated in the laboratory from natural Lake Mir samples (white circles); Table 2). The best fit linear regression line is shown; its parameters are in the text.

the inorganic iodine species, iodate and iodide. Finally, this fractionation was found to apply to organic compounds of phosphorus, nitrogen and carbon. Although preliminary, this result is sufficiently original and of note in itself to warrant promulgation to other workers because it points towards a resolution of the established deficit in the supply of iodine from the oceans to the atmosphere (Jones et al., 2010). The marked indifference of iodide towards foam-creation in the current experiments high-lights the fact that org-I brings special properties to the problem. This is a key factor, as Chapman and Liss (1981) effectively reported the same thing when they discovered that there was no significant accumulation of inorganic-I (iodate and iodide) in the surface micro-layer of the ocean. Given the above, it is pertinent to consider the intimate nature of the experiments, to link them to existing experience in other scientific domains, before widening to the larger issue of the global cycling of iodine.

5.2. The results accord with wider, industrial and environmental experience of foams

As stated, during this work it seemed likely that an important difference between natural and artificial foams, and indeed between one natural foam and another (Table 2), would lie in the extent to which the foam stands before it is sampled. During any standing period, bulk water occluded within the foam will drain away, leaving the foam more enriched in the compounds which constitute the bubble sheath. This is presumably a gravitational effect somewhat similar to that which allows freshwater-ice to grow out of the surface of Polar Seas, when the salt-rich mother-liquor drains downwards from the newly frozen water, back into the sea. Our assumptions about drainage are generally borne out by the literature on the use of foam as a general separation technique in the production of modern organic chemicals (see: Clarkson et al., 2000; Martin et al., 2010). In the past, the separation of an organic compound from both its parent compounds and any by-products formed during its synthesis, was managed conventionally by a technique such as distillation. With an increase in interest in the synthesis of exotic compounds, many of which are either thermo-labile, otherwise easily decomposable, or exhibit other properties which makes separation difficult, newer techniques have been devised. One of these is foam separation, whereby organic compounds with some surfactant property are literally lifted out of their mother-liquor, up into a receiver column, simply by the blowing in of air, or other gas, into the liquid. Moreover, in this way even organic compounds without any surfactant property can sometimes be co-separated, together with a better surfactant, added solely to provoke foam generation. But, to return to the main point of this aside into industrial chemistry, it is now well-known that the longer the time which the newly formed foam can stand before it is harvested, the more the fractionation increases. In the future such industrial experience may become useful in environmental science as many industrial experiments will probably have ranked the relative susceptibility of different groups of compounds, to fractionation. Such practical experience is also borne out in more general theory (see: Schilling and Zessner, 2011) where foams are described as being thermodynamically unstable due to their high interfacial energy. Kinetically, their instability is classified into unstable or transient foams with lifetimes of seconds, and metastable, or so-called permanent foams, with lifetimes of hours to days.

It is clear from the above that the surfactant coating around a bubble will be an important consideration for the observed enrichment of natural and laboratory generated foams with organic iodine – indeed, it would be interesting to know, for example, whether the org-I compounds are themselves surfactants, or whether they are instead co-separated. This will depend considerably upon the nature of the organic matter produced in the seas

and oceans. It is already well-established that foaming events in the oceans become extreme when high wind-strength coincides with the immediate aftermath of an algal bloom which has released much organic matter into the water. Such intensive foaming has been reported, for example: around kelp beds on the South African west coast (Velimirov, 1982); in the North Sea and Eastern English Channel (Bätje and Michealis, 1986; Desroy and Denis, 2004; Seuront et al., 2006) after blooms of *Phaeocystis* sp.; in the Barents Sea (Druzhkov et al., 1997), and around the Pacific Ocean Island of Cano after dinoflagellate blooms (Guzmán et al., 1990). Further information about the org-C and org-I compounds involved in such events would be useful. Meanwhile, the fact that the I/C mole ratio of $2.9 (\pm 0.2) \cdot 10^{-4}$ for the foams from Lake Mir is close to the literature values of $(1.0\text{--}1.6) \cdot 10^{-4}$ for I/C assimilation ratios in seston in the Pacific Ocean (Elderfield and Truesdale, 1980) and coastal Antarctic Ocean (Chance et al., 2010) is consistent with the organic compounds being formed in situ in the water (autochthonous) rather than imported from elsewhere (allochthonous). It is also of note that this ratio is also comparable to org-I/DOC ratio of $2.6 (\pm 1.1) \cdot 10^{-4}$ ($n = 23$) in the water column of an anchialine cave system, where organic iodine seems to originate from the karst (Žic et al., 2011; Cuculić et al., 2011).

The frit used in this work to generate foam was chosen arbitrarily, it being already available in the laboratory. Nevertheless, the obvious success achieved with it shows that while foam separation as a process might well be tuned by generating of an optimal bubble-size (see: Keene et al., 2007; Fuentes et al., 2010), the process is easy to demonstrate crudely. Moreover though, our experiments prompted us to consider the possibility that bubbles of air (in air) might behave differently to bubbles of air (in water). The bubbles produced in the foaming experiments did not burst immediately at the surface, but rather collected on top of the surface. Given extreme foaming events such as those mentioned above there can be little doubt that the presence of surfactants (Seuront et al., 2006; Schilling and Zessner, 2011) will induce the bubbles to persist longer as a foam, rather than to burst immediately as they appear at the surface. Moreover, the rupture of such longer-lived bubbles can be expected to yield a somewhat different result than short-lived ones because the mother-liquor will have had time to drain-off. MacIntyre (1974) reviewed some key aspects of bubble drainage, and it is clear that a great deal of complex physics is involved.

5.3. Models of bubble-bursting

Most early accounts of bubble bursting in the biogeochemical context relate to air bubbles (in water) of between about 50 and 1500 μm diameter, produced as a breaking wave entrains air as it plunges up-wind, into a trough. On surfacing again, and after the wave passes, the bubbles remain on the water until they burst. Fast action photography with dyed-water revealed (MacIntyre, 1972; Duce and Hoffman, 1976) that the material in the droplets is derived from a 0.025–0.75 μm layer of the inner surface of the bubble, with the first one containing a greater proportion of the inner lining of the bubble, than do subsequent droplets. This mode of bubble formation has been used for several decades to explain how a major contribution of sea-salt is made to the atmosphere from the sea, and hence to rain and other precipitation, and therefore eventually to river water.

A casual examination of the many high-speed videos of soap bubbles, now available on the worldwide web, shows that a soap-bubble punctured by a relatively tiny missile or pin-prick, leads to an unravelling of the soap film, as surface-tension within the sheath is relaxed, and the material that made up the sheath is shattered into many tiny particles. The facts about bubble behaviour that were cutting-edge science in the 1960s are therefore now so much

easy to appreciate. The particles created when an air-bubble (in air) bursts are very much finer than those produced when an air bubble (in water) bursts. Applied to bubbles on water, the latter explains how it is that the upper, air–air surface which first shatters into finer particles – the film droplets (Spiel, 1998; Day, 1964) – and secondly then, that the subsequent relaxation of tension in the air–water interface of the bubble (colloquially the bottom surface) which then produces the jet-droplets.

Spiel (1998) explains that, contrary to earlier reports, films of all bubbles up to at least 14.6 mm diameter burst in an orderly fashion when a hole appears, usually at the film's edge, and propagates through the film, gathering up its mass into a toroidal ring. After establishing that film droplets are of meteorological significance, Day (1964) reports that the number of film droplets produced is dependent on bubble size, ranging from none for 0.1 mm diameter bubbles to 300–400 for 4 mm diameter bubbles in salt water, and that larger numbers of film droplets are produced when bubbles burst in three percent NaCl solution than in filtered seawater, and significantly larger numbers are produced in saline than in distilled water. Moreover, quoting Cipriano and Blanchard (1981), Massel (2007) states that a large proportion of the film-droplets in seawater will have a diameter $< 0.02 \mu\text{m}$. It was further reported that only bubbles larger than 2.4 mm diameter can launch film droplets by this means. Massel (2007) explains, presumably importantly, that not all of the film-droplets will have a high enough velocity to eject them into the aerosol. The subject is obviously complex and the above references merely outline some of the major findings. Of immediate concern though, is whether or not the film droplets can participate significantly in aerosol formation.

5.4. The use of elemental ratios to simplify foam enrichments

Our assumptions about the drainage of foams was generally validated by our study of the elemental ratios of the foam contents. More specifically, from this perspective the artificial foams resembled the natural ones much more closely, since, for any two elements captured within a draining foam, their ratios would be expected to remain relatively constant. This is readily understandable in terms of fractionations both for I and P, where in addition to Eq. (1):

$$F(P)_{\text{Cl}} = \frac{\left(\frac{[P]}{[Cl]}\right)_{\text{atm}}}{\left(\frac{[P]}{[Cl]}\right)_{\text{sw}}} \quad (3)$$

So that, dividing Eq. (1) by (3):

$$\begin{aligned} \frac{F(I)_{\text{Cl}^{-1}}}{F(P)_{\text{Cl}^{-1}}} &= \frac{\left(\frac{[I]}{[Cl]}\right)_{\text{atm}} \div \left(\frac{[P]}{[Cl]}\right)_{\text{atm}}}{\left(\frac{[I]}{[Cl]}\right)_{\text{sw}} \div \left(\frac{[P]}{[Cl]}\right)_{\text{sw}}} \\ &= \frac{\left(\frac{[I]}{[P]}\right)_{\text{atm}}}{\left(\frac{[I]}{[P]}\right)_{\text{sw}}} = F(I)_P \end{aligned}$$

that is, the fractionation of I relative to P, $F(I)_P$.

The similarity in the behaviour of organic forms of the elements I, N and P is consistent with the likelihood of longer-chain or

complex molecules, such as exudation or decomposition products of phytoplankton, being involved as surfactants (Schilling and Zessner, 2011). However, notice should perhaps also be taken of MacIntyre's (1974) statement of a notable difference between iodine and phosphorus, that inorganic phosphate can attach itself to organic matter. This supports our observation that iodide, the only inorganic form of iodine present at significant concentrations in Mir water, was not enriched by the foam-making process, but it does perhaps complicate the story behind fractionation of iodine relative to phosphorus, $F(I)_p$. The result similarly matches that of Chapman and Liss (1981), who reported little or no micro-layer enrichment in inorganic forms of iodine or nutrient species in North Sea coastal samples.

5.5. On the similarity between the foams from the three different marine environments and the link to the ocean surface

The similarity between the foams encountered in the three different, oligotrophic to eutrophic, marine environments examined: Lake Mir (Carić et al., 2010; Žic et al., 2012), Krka Estuary (Louis et al., 2009), and the second marine Lake, Velike Soline (Carić et al., 2011) (Table 2), shows that transport and concentration of organic iodine by foam is not unique to Lake Mir, but instead, is a common process. There seems to be little reason to suspect that Croatian bubbles should be that much different than those from ocean environment, particularly since Krka Estuary is an oligotrophic environment, with dissolved organic carbon concentration of up to around $80 \mu\text{mol l}^{-1}$ (Louis et al., 2009). As these low concentrations meet those generally obtained from oceanic environments ($60\text{--}90 \mu\text{mol l}^{-1}$) (Libes, 2009), and, similarly, org-I comprises only about 14% of total iodine (Table 1), similar fractionations may well be encountered with oceanic foams. Additionally though, this suggest that the actual concentration of organic compounds in the bulk water is not a prerequisite to obtain high fractionations (Table 2). Finally, since the bubbles breaking on the sea surface each year will collect some 2 Gt of carbon during their rise to the ocean surface (Monahan, 2001) a substantial fraction of organic iodine will be available to air-sea transport.

5.6. Conclusions and the wider context of the marine aerosol literature

As indicated, our observation of major fractionation of org-I during formation of foam on Lake Mir and other Croatian waters, as well as reporting on a local phenomenon, is potentially important in explaining the air-sea exchange of higher molecular weight org-I.

As suggested here, previous models of the gas/aerosol interactions of the element iodine are unable to sustain the concentration levels of the radical IO observed in the field. These models rely heavily upon iodoalkanes to supply the required iodine, and upon the presence of soluble organic-I sorbed to a matrix composed of various iodine oxides. Meanwhile, older literature (e.g., Seto and Duce, 1972) showed that relatively higher molecular weight org-I compounds, synthesised in, and extracted from a culture of *Phaeodactylum* sp., were fractionated relative to the major constituents of seawater, during simulated aerosol production by the bubble bursting approach. This literature, and its suggestion of the presence of relatively high molecular weight org-I in the marine aerosol perhaps, for example, di-iodo-tyrosine, seems to have been ignored in the aforementioned modelling literature. Other, more recent relevant knowledge of organic chemistry, is that organic compounds which have little or no surfactant properties themselves, can be co-separated by bubbling with surfactants. This can be added to the conclusions of Seto and Duce (1972). It thereby

provides even greater ability for relatively high molecular weight org-I to be co-separated from seawater salts, together with the greater proportion of organic matter in seawater that, in any case, may be fractionated into the aerosol during the bursting of bubbles. The fractionation of iodine onto an aerosol, relative to the major constituents of seawater, is greatest on the smaller aerosol particles collected. The previous bubble-bursting mechanism of the 1970s only includes particles created as jet-drops. MacIntyre (1974) specifically denies any role to the smaller film-droplets which accumulate from the shattering of the hemisphere of the bubble that provides the air-to-air interface. Although the complex physics on which this is based is outside the present discussion, after re-examination, it might still offer further leverage towards a greater contribution of org-I to the aerosol.

The present study only offers circumstantial evidence of the involvement of the bubble bursting mechanism. That is, it tends to establish a conclusion by inference from known facts which are otherwise hard to explain (Sykes, 1976). Hence it is indirect evidence which forces one to towards a conclusion which, perhaps, one is reluctant to accept. So, given the previous knowledge of fractionation and bubble bursting, together with ideas about co-separation, it is very hard to explain why the marine aerosol would not contain relatively high molecular weight org-I compounds taken up by bubble bursting. This is compounded by the observation that iodide was not fractionated in the experiments carried out here, while the concentrations of neither iodate nor iodide are enhanced in the marine micro-layer (Chapman and Liss, 1981). Incidentally, the Seto and Duce (1972) experiment itself was also only able to produce circumstantial evidence. Therefore, direct evidence of the presence of several relatively high molecular weight org-I compounds in both the sea and the aerosol is required.

Our results support those of Murphy et al. (1997), obtained from laser ionisation spectrometry at Cape Grim, Tasmania, who report the presence of two enrichments in the aerosol: a moderate one in many particles and a few I-rich particles. They identify a correlation between iodine and organics as clearly consistent with org-I, but that this does not preclude deposition of iodine from the gas phase. Meanwhile, at the same site but with a somewhat different instrument, Middlebrook et al. (1998) report finding sea-salt compounds mixed with organics in over half of the particles studied. They also report that when the sodium sulphate content was low, iodine correlated well with the organics, which is consistent with the bubble bursting mechanism. Baker et al. (2000) suggested that iodine in the aerosol is probably present in varying proportions as soluble inorganic iodine, soluble organic iodine (SOI), and insoluble or unextractable iodine. Higher molecular weight org-I taken up by bubble bursting seems likely to fall into the latter two categories, depending upon the precise definition of insoluble, which is presumably an operational one. Baker (2005) followed up the SOI explanation with analysis of aerosols from two cruises on the Atlantic Meridional Transect (AMT) programme. He concluded that it is difficult to calculate an Enrichment Factor for SOI in the aerosol because of the relatively small amount of data available for dissolved organic iodine concentrations (DOI) in seawater. Nevertheless, he conjectured that this enrichment would be greater than for inorganic iodine. We suggest that our current experience in Lake Mir and elsewhere, described here, is the closest vindication so far available for Baker's (2005) conjecture. Finally, as O'Dowd et al. (2004) has pointed out, it is difficult to understand aerosols without acknowledging that up to 45% of the mass of the sub-micrometre component can be water-insoluble organic matter, together with another 18% of water soluble organic matter. Given our experience of marine foam, albeit from an unusual location, it is hard to neglect the possibility that much of O'Dowd et al's. (2004) organic matter is also not org-I.

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