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Journal

Environmental Chemistry, 2(4)

ISSN

1448-2517

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Publication Date

2005

DOI

10.1071/en05072

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Peer reviewed

Marine Organic Halide and Isoprene Emissions Near Mace Head, Ireland

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Environmental Context. Atmospheric aerosols have received increasing attention, not only because they include cloud condensation nuclei, essential for precipitation, but also because of their absorption and scattering of radiation, which may affect climate. The process of aerosol formation, however, is not well understood. This paper describes measurements of the fluxes into the atmosphere of several possible biogenic precursors to primary aerosol production.

Abstract. Vertical profiles of the concentration of several alkyl halides, as well as isoprene, were made from the surface to 200 m, using a tethered balloon platform, near Mace Head, Ireland in September–October 2003. Profiles indicate a surface source of several alkyl halides. Alkyl halides have been proposed as a source of new particles in the atmosphere. Estimates of emission rates ($\mu\text{g m}^{-2} \text{h}^{-1}$) were made using a flux-gradient technique for CH_2Br_2 (0.8), CHBr_3 (6), CH_2IBr (0.1), CH_2I_2 (0.1), and isoprene (24).

Keywords. aerosols — alkyl halides — biogenic emissions — iodine

Manuscript received: 9 September 2005.

Final version: 25 October 2005.

Episodic new particle formation has been reported in coastal regions, especially at low tide, when vegetation (primarily macroalgae) is exposed directly to the atmosphere during daytime. New particle formation is generally thought to occur through binary nucleation of sulfuric acid or ternary nucleation of H_2SO_4 , H_2O , and NH_3 . However, in coastal areas, sulfuric acid does not correlate with new particle formation or tidal cycles.^[1,2] The measurement of iodine in the ultrafine particle composition^[3] during coastal nucleation events has focused attention on organic and inorganic emissions from seaweed as potential iodine sources. Molecular iodine^[4] and CH_2I_2 ^[5] are likely precursors, since they rapidly photolyze to give iodine atoms, which are converted to the IO radical by reaction with ozone. IO is further oxidized to higher iodine oxides which are less volatile and can either condense on pre-existing stable clusters or form new particles.^[5]

Macroalgae emissions of alkyl iodides were measured at Mace Head, Ireland^[3] from enclosures of several species, but the plant-level emissions were not extrapolated to an area source. Other possible sources were not identified. Molecular iodide has also been measured over the ocean at Mace Head.^[4] In this paper, we describe an experiment where concentration gradients of alkyl halides and other biogenic compounds from coastal marine biota were measured from the surface up to 200 m using a tethered balloon profiling

system. A surface layer gradient flux technique was applied to estimate fluxes of biogenic volatile organic compounds in the coastal area.

Balloon meteorological and chemical profiles were measured at two locations on the west coast of Ireland: the Mace Head Atmospheric Research Station (MH, $53^\circ 19' 34''\text{N}$, $9^\circ 53' 14''\text{W}$) near Carna, county Galway (more than 5 m above sea level and 50 m from the coast at high tide) from 19 to 21 September, 2003 (7 profiles) and the Martin Ryan Institute (MRI), approximately 5 km east of MH (on a flat peninsula at sea level approximately 20 m from the shoreline at high tide) from 23 September to 1 October, 2003 (19 profiles). The MH location was exposed to open ocean to the north, west and south and the balloon was launched at the observatory, which sits atop a cliff overlooking the ocean; the MRI site was bounded north and south by tidal flats as close as 200 m to the site and open ocean immediately to the west. The balloon was launched at approximately sea level.

Meteorological profiles of wind direction, wind speed, temperature, and humidity were measured on the tethered balloon platform using an AIR tethersonde system (Atmospheric Instrumentation Research, Boulder, CO, USA; model P1-5A).

Additional meteorological data were obtained from the Mace Head Meteorological Facility (<http://macehead.physics.nuigalway.ie>).

The tethered balloon sampling system and analytical details have been described in detail previously.^{16,71} Volatile organic compounds (VOCs) were collected onto solid absorbent cartridges using a microcomputer-based sampler. The samplers logged sample collection flow rates, pressure altitude, temperature and humidity. Individual samplers were deployed on the balloon tether-line at altitudes of approximately 50, 100, and 200 m in most deployments. Additional samplers were also deployed at approximately 0.5 m above ground level simultaneously with balloon profiles or at other selected times. All sampling times were 30 min.

Sampled cartridges were returned to the NCAR, Boulder, Colorado laboratory for thermal desorption gas chromatography–mass spectrometric (GC–MS) analysis. Details of the analysis have been provided previously.^{17,81} The absorbent collection and analysis techniques are similar to those used previously to measure alkyl halides at MH.¹³¹ Samples volumes were of the order of 6 L. Compounds routinely monitored for this experiment included CH₃CH₂Br, CH₃CH₂I, CH₂Br₂, CH₂ICl, CH₂BrI, CHBr₃, CH₂I₂, isoprene, and monoterpenes.

Calibrations were made with respect to compressed gas standard (15000 kPa) containing all alkyl halides monitored (approximately 50–100 ppb each component; working standards were prepared by dynamic dilution); the calibration standards and procedure have been described previously.¹⁸¹ Isoprene and terpene calibrations were made with respect to another compressed gas standard of approximately 10 ppb each of isoprene and camphene in nitrogen; the quantization of this standard was made by comparison with a primary standard through GC–FID analysis.

The uncertainties in the calibration standards for individual trace gases were estimated at approximately 5% for ethyl bromide (EtBr), ethyl iodide (EtI), CH₂Br₂, and CHBr₃, isoprene and α -pinene and 15% for CH₂I₂, CH₂BrI, and CH₂ICl. Uncertainties in the volume sampled were dependent primarily on the individual flow meters used in each sampler, which were accurate to approximately 10%. Overall uncertainties of concentrations were determined by propagation of errors: EtBr, EtI, CH₂Br₂, and CHBr₃, isoprene and α -pinene uncertainties were of the order of 15%; CH₂I₂, CH₂BrI, and CH₂ICl uncertainty was of the order of 25%, due to generally lower concentrations measured and greater uncertainty in the concentration of the calibration standard.

A summary of median surface concentrations (and interquartile ranges) for selected VOCs at the MH and MRI sites are given in Table 1. Concentrations of most VOCs reported here were similar at the two sites. The surface winds at each site were determined by the local sea breezes during daytime (when all balloon profiles were made).

Concentrations of the biogenic VOC emissions from surface data did not appear to be correlated with wind speed. For emissions from sea surface water, higher emissions at higher wind speed would be expected.¹⁹¹ Higher winds, however, would dilute concentrations of ocean or exposed seaweed emissions. Continuous diurnal sampling was not made (most sampling occurred during daylight hours 0900–1700) and diurnal concentration variations cannot be described. Previous reports¹¹⁰¹ showed increased concentrations of CH₂I₂, CHBr₃, CH₂I₂Br, and CH₂ICl during daytime at low tide.

Correlations of concentrations were observed among various emissions: CH₂I₂ : CH₂I₂Br ($R^2 = 0.7$); CH₂I₂ : CHBr₃ ($R^2 = 0.3$); CH₂I₂ : CH₂ICl ($R^2 = 0.2$); similar correlations have been reported previously.¹¹⁰¹ Monoterpenes concentrations were also significantly correlated ($R^2 = 0.8$ for α -pinene : camphene).

Median profiles for several VOCs at MRI are shown in Fig. 1 and the median concentrations and interquartile ranges (central 50%) of concentrations are listed in Table 2. Local sources for CH₂Br₂, CH₂ICl, CH₂BrI, and CH₂I₂, and isoprene may be inferred from vertical gradients of decreasing concentration with height. In contrast, the profiles for EtBr, EtI, and α -pinene have similar shapes: nearly constant concentrations with altitude, with somewhat lower concentrations at the surface; this suggests a source outside the footprint or a non-homogeneous source within the footprint of the profile.

A comparison of concentrations recently measured at Mace Head in May 1997¹¹⁰¹ indicates good agreement between present and previous measurements for all alkyl halides, except for ethyl bromide and ethyl iodide, which are approximately a factor of ten higher from this study. It is possible that the warmer water during this experimental period (September) may have stimulated increased emissions, since productivity and emissions generally increase with environmental temperatures.¹¹¹¹

Seaweed (macroalgae) present in the Mace Head area has been identified as a source for several alkyl halides: CH₂Br₂, CHBr₃, and CH₂I₂.¹³¹ CH₂I₂, CHBr₃, and CH₂ICl concentrations are reported to increase at low tide, when more of the macroalgae are exposed to air. CH₂BrI and CH₂ICl may be Br and Cl substitution products from CH₂I₂ in sea water.¹¹⁰¹ Additionally, isoprene emissions may be inferred from the gradients measured. Isoprene is the dominant biogenic VOC emitted from terrestrial ecosystems and is also a major VOC constituent in the marine boundary layer.¹¹²¹ Isoprene is emitted directly by phytoplankton and may be indirectly produced by zooplankton grazing.¹¹¹¹ Monoterpenes, including α -pinene, β -pinene, camphene and limonene, as well as more minor contributions from other terpenes, are also measured

Table 1. Surface median concentrations and interquartile range (central 50% of measurements), parts per trillion by volume (ppt), at the Mace Head and Martin Ryan Institute sampling sites

Site	EtBr	EtI	CH ₂ Br ₂	CH ₂ ICl	CH ₂ I ₂ Br	CHBr ₃	CH ₂ I ₂
MH	3 (1–6)	2 (2–4)	3 (2–3)	0.1 (0.1–0.3)	0.1 (<0.1)	14 (12–18)	0.2 (0.1–0.4)
MRI	2 (1–3)	1 (0.4–2)	1 (1–2)	0.05 (<0.2)	0.1 (<0.2)	10 (4–19)	0.2 (0.1–0.4)

in all air samples, but the vertical gradient indicates that they likely have a different source from the alkyl halides.

Gradients of decreasing concentration with altitude (Fig. 1) indicate that several of the alkyl halides have local surface sources, such as the seaweed species previously identified.^[13] An approximation of the magnitude of the fluxes is made by a surface layer gradient technique,^[14] where the estimated flux is a function of the product of the eddy diffusivity and the concentration gradient of individual VOCs. The surface layer gradient flux technique assumes conditions of neutral stability, associated with moderate to high wind and low sensible heat flux, such as the conditions at Irish coast during these experiments. The eddy diffusivity, K , is estimated^[15] as the product of $k \times u^* \times z$, where k is von Karman's constant (0.4), z is the altitude in the atmosphere at which estimate is made, and u^* is the friction velocity; u^* , in turn, is estimated as the square root of the product of the drag coefficient, C_d ($1.1\text{--}1.4 \times 10^{-3}$ over water^[15]) and U^2 , the wind speed at altitude, measured on the balloon meteorological system.

Fluxes of VOCs from the coastal area are estimated from concentration gradients measured at the MRI site, situated in

an extensive flat area at approximately sea level. The concentration gradient between 50 and 100 m is used to estimate fluxes, instead of from the surface to 50 m. The flux footprint of the emissions has been estimated to extend approximately ten times the height of sampling, with the largest percentage of the flux contributed by the areas closer to the measurements point.^[16] The footprint of air sample measurements at different altitudes included some percentages of open water, tidal basins, rocky, barren coastline, grassland, etc. The distribution of macroalgae is not uniform in area or species and the exposed distribution changes dramatically with tides. Since the seaweed distribution is not homogeneous, measurements at 50 m are thought to average the surface source somewhat. Measurements at 200 m are not used in the flux calculation, since the footprint at this altitude probably includes a large area of open ocean; 200 m may at times be above the constant flux surface layer. Winds at 50 and 100 m were, on average, of the same magnitude ($5 \pm 2 \text{ m s}^{-1}$). The calculated eddy diffusivity is in the range from 4 to $7 \text{ m}^2 \text{ s}^{-1}$.

Emission fluxes are estimated (in units of $\mu\text{g VOC m}^{-2} \text{ h}^{-1}$) for CH_2Br_2 (0.8), CH_2I_2 (0.1), CH_2BrI (0.1), and CHBr_3 (6). Additionally, an isoprene emission flux

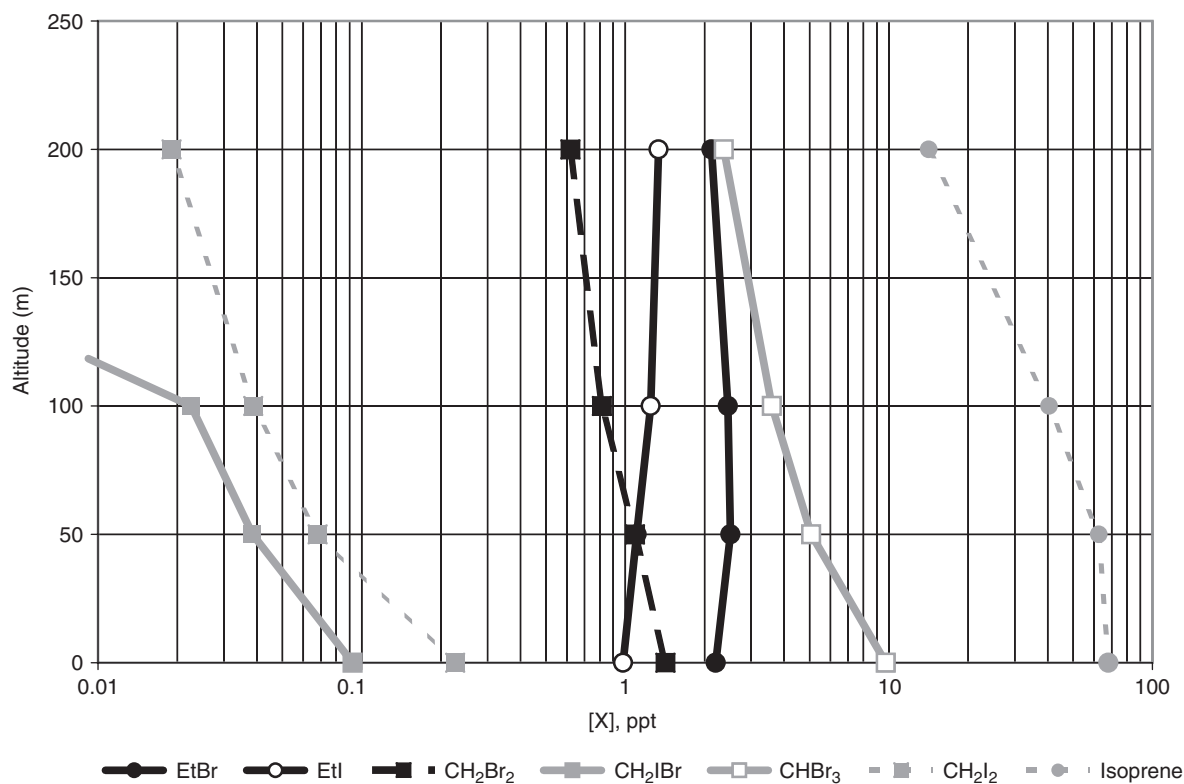


Fig. 1. Median concentration profiles for selected volatile organic compounds from the Martin Ryan Institute.

Table 2. Median and interquartile range of concentrations (ppt) measured at typical sampling altitudes (m)

Altitude	Isoprene	EtBr	EtI	CH ₂ Br ₂	CH ₂ I ₂	CH ₂ BrI	CHBr ₃	CH ₂ I ₂	α -Pinene	Camphene
0	68 (10–160)	1 (3–8)	1 (0.4–2)	1 (0.7–2)	0.05 (0.02–0.1)	0.1 (0.01–0.2)	10 (4–20)	0.2 (0.1–0.4)	4 (2.7)	1 (1–4)
50	63 (7–210)	6 (4–11)	1 (0.6–2)	1 (0.9–1.2)	0.04 (0.3–0.6)	0.04 (<0.06)	5 (3–6)	0.1 (0.01–0.1)	5 (4–9)	1 (1–4)
100	41 (7–270)	6 (5–8)	1 (0.9–3)	0.8 (0.6–1)	0.04 (0.02–0.07)	0.02 (<0.04)	4 (3–5)	0.04 (0.02–0.9)	6 (5–9)	2 (1–8)
200	14 (4–130)	5 (4–8)	1 (0.9–3)	0.6 (0.4–0.8)	0.03 (0.02–0.4)	0 (<0.01)	2 (2–3)	0.02 (0.01–0.4)	5 (4–6)	0.9 (0.2–6)

of approximately $24 \mu\text{g m}^{-2} \text{h}^{-1}$ is also estimated. Ethyl bromide and ethyl iodide gradients do not indicate local emissions from the same source as other alkyl halides.

The biogenic VOCs measured are either chemically or photolytically destroyed in the atmosphere. Atmospheric lifetimes with respect to these processes vary with individual VOC from minutes (CH_2I_2 , ~ 4 and CH_2IBr , ~ 60 min) to days.^[17] The calculated emission fluxes for CH_2I_2 and CH_2IBr may represent an upper limit to their fluxes, as chemical losses will act to increase the concentration gradient with altitude.

Alkyl halide emission rates have been reported^[3,18] as a function of leaf area or weight for seaweed species common at Mace Head and include rates for CH_2Br_2 , CHBr_3 , CH_2IBr , and CH_2I_2 . The distribution of the dominant species of macroalgae on the Irish coast was used to calculate seawater concentrations of several alkyl halides emitted,^[18] which compared reasonably well to measured seawater concentrations. Emissions into the atmosphere may be inferred for exposed macroalgae, using their estimate of the distribution of macroalgae at low tide. Calculations indicate significantly (an order of magnitude) higher fluxes than derived from the balloon profile measurements. The calculated eddy diffusivity is of the order of that previously determined^[18] and analytical uncertainties in the surface layer gradient technique are not sufficient to account for the difference. Gradients of alkyl halides used in the flux estimates were measured at all tide levels, and, consequently, may result in lower average fluxes. However, the seaweed emission data include a large range (more than an order of magnitude) of emission factors for individual species with no information on percentage species composition; the emission rate estimates are, therefore, also highly uncertain.

Several important research activities are indicated from this limited study. The distribution of alkyl halide emitting species is important in predicting areas of likely new particle formation. The seasonal cycle of these emissions and the physiological parameters that affect emissions have also not been sufficiently characterized to allow the emissions to be modeled adequately. Consequently, the impact of reactive iodide emissions into the atmosphere on new particle formation is only roughly approximated at present.

Acknowledgements

We thank the National University of Ireland for the use of the facilities at the Mace Head Atmospheric Research Station and

for support of our research activities, the Martin Ryan Institute for hosting part of our study, and E. Atlas, who provided calibration standards. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research and is sponsored by the National Science Foundation.

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