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 \( \text{CH}_2\text{Br}_2 (0.8) \), \( \text{CHBr}_3 (6) \), \( \text{CH}_2\text{IBr} (0.1) \), \( \text{CH}_2\text{I}_2 (0.1) \), and isoprene (24).

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The tethered balloon sampling system and analytical details have been described in detail previously.\(^6\) 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.\(^7\) The absorbent collection and analysis techniques are similar to those used previously to measure alkyl halides at Mace Head.\(^3\) Samples were volumes of the order of 6 L. Compounds routinely monitored for this experiment included CH\(_2\)Cl\(_2\), CH\(_2\)I\(_2\), CH\(_3\)Br\(_2\), CH\(_2\)I\(_2\), CH\(_3\)I\(_2\), CH\(_3\)BrI, CH\(_3\)ICl, CH\(_3\)Br\(_3\), CHI\(_3\)Br, CHI\(_2\)I, and CHIBr\(_3\). Measurements of ethyl bromide (EtBr), ethyl iodide (EtI), isoprene, and CH\(_2\)I\(_2\), iso-prene, 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.\(^8\) 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), CH\(_2\)Br\(_2\), and CHBr\(_3\), isoprene and α-pinene and 15% for CH\(_3\)I\(_2\), CH\(_3\)Br\(_1\), and CH\(_2\)I\(_2\). 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, CH\(_2\)Br\(_2\), and CHBr\(_3\), isoprene and α-pinene uncertainties were of the order of 15%; CH\(_3\)I\(_2\), CHBr\(_3\), and CHBr\(_3\) I\(_2\) 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 to 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.\(^9\) 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 reports\(^10\) showed increased concentrations of CH\(_2\)I\(_2\), CHBr\(_3\), CHI\(_2\)Br, and CH\(_3\)ICl during daytime at low tide.

Correlations of concentrations were observed among various emissions: CH\(_2\)I\(_2\) : CH\(_2\)I\(_2\) (R\(^2\) = 0.7); CH\(_3\)I\(_2\) : CHBr\(_3\) (R\(^2\) = 0.3); CH\(_3\)I\(_2\) : CH\(_2\)I\(_2\) (R\(^2\) = 0.2); similar correlations have been reported previously.\(^10\) 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 CH\(_2\)Br\(_3\), CH\(_2\)I\(_2\), CHBr\(_3\), and CH\(_3\)I\(_2\), and isoprene may be inferred from vertical gradients of decreasing concentration with height. In contrast, the profiles for EtBr, EtI, 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 1997\(^10\) 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.\(^11\)

Seaweed (macroalgae) present in the Mace Head area has been identified as a source for several alkyl halides: CH\(_2\)Br\(_3\), CH\(_2\)Br\(_3\), and CH\(_2\)I\(_2\).\(^3\) CH\(_3\)I\(_2\), CHBr\(_3\), and CH\(_3\)I\(_2\) concentrations are reported to increase at low tide, when more of the macroalgae are exposed to air. CH\(_2\)BrI and CH\(_2\)I\(_2\) may be Br and I substitution products from CH\(_2\)I\(_2\) in sea water.\(^10\) 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.\(^12\) Isoprene is emitted directly by phytoplankton and may be indirectly produced by zooplankton grazing.\(^11\) Monoterpenes, including α-pinene, β-pinene, camphene and limonene, as well as more minor contributions from other terpenes, are also measured.

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**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\(_2\)Cl | CH\(_3\)I\(_2\) | CHI\(_2\)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) |

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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. An approximation of the magnitude of the fluxes is made by a surface layer gradient technique, where the estimated flux is a function 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 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, $C_d$ (1.1–1.4 × 10$^{-3}$ over water), 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. 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 m$^2$ s$^{-1}$.

Emission fluxes are estimated (in units of $\mu$g VOC m$^{-2}$ h$^{-1}$) for CH$_2$Br$_2$ (0.8), CH$_2$I$_2$ (0.1), CH$_2$BrI (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.](image_url)

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

| Altitude (m) | Isoprene | EtBr  | EtI   | CH$_2$Br$_2$ | CH$_2$I | CH$_2$BrI | CHBr$_3$ | CH$_2$I$_2$ | $\alpha$-Pinene | Camphene |
|-------------|----------|-------|-------|--------------|---------|-----------|----------|-------------|----------------|----------|
| 0           | 68 (10–160) | 1 (3–8) | 0.4–2 | 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 (1.6–2) | 0.7 (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)  | 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)  | 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\(_2\)I, \(~\sim 4\) and CH\(_2\)IBr, \(~\sim 60\) min) to days.\(^{17}\) The calculated emission fluxes for CH\(_2\)I and CH\(_2\)IBr 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\(_2\)Br\(_2\), CHBr\(_3\), CH\(_2\)IBr, and CH\(_2\)I\(_2\). The distribution of the dominant species of macroalgae on the Irish coast was used to calculate seawater emissions from the same source as other alkyl halides. Atmospheric bromide and ethyl iodide gradients do not indicate local exposure rates of macroalgae, using their estimate of the distribution 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.

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