

Seasonal variations of dissolved alkenes in coastal waters

N. Gist^{a,c,*}, A.C. Lewis^{b,c}

^a Plymouth Marine Laboratory, Prospect Place, Plymouth, PL1 3DH, UK

^b Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

^c Department of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

Received 22 March 2005; received in revised form 15 September 2005; accepted 5 October 2005

Available online 22 December 2005

Abstract

Quantitative sea–air fluxes are needed for accurate global budget estimations of the short-chain non-methane hydrocarbons, but the processes that affect their production are not currently fully understood. We measured concentrations of ethene and propene at a North Sea coastal site (Scarborough, North Yorkshire, UK, 54.3°N 0.4°W) over a full year, and demonstrate that their marine concentrations, and the processes controlling their production, are heterogeneous. Seasonal cycles were observed for the alkenes, with a summer maximum, and concentrations varying over an order of magnitude, from 17 to 951 pmol l⁻¹ for ethene, and from 13 to 330 pmol l⁻¹ for propene. There was also significant heterogeneity in the alkene concentrations during the spring and summer months. Inferred sea–air fluxes of the alkenes (calculated from measured seawater concentrations, a set of clean air concentrations and windspeeds at the time of sampling) increased in summer, driven by increases in seawater concentrations. Fluxes ranged over an order of magnitude, which highlights the importance of considering temporal variations for annual global flux estimates. In a laboratory-based study of the production of ethene and propene under UV irradiation, alkene production was induced at net rates ranging from 0.10–0.18 pmol l⁻¹ min⁻¹, and the rate of production was dependent on the light flux incident on the water. © 2005 Elsevier B.V. All rights reserved.

Keywords: Ethene; Propene; NMHC; Non-methane hydrocarbons; Seasonal variations; Photochemistry; Air–sea interaction; UK, North Yorkshire, Scarborough, South Bay

1. Introduction

Non-methane hydrocarbons (NMHCs) play a key role in atmospheric chemistry, affecting atmospheric concentrations of the hydroxyl radical and ozone. The majority are terrestrial in origin, but the sea acts as an additional source for the light NMHCs (see for example [Bonsang et al., 1988](#); [Plass-Dulmer et al., 1995](#); [Broadgate et al., 1997](#)). Emission of NMHCs to the atmosphere is probably the major loss mechanism from the

surface ocean ([Plass et al., 1992](#); [Riemer et al., 2000](#)), so their near-surface seawater concentrations depend both on rates of production and on rates of ocean–atmosphere chemical exchange. The rate of this exchange, the sea–air flux, has been inferred previously from seawater concentrations coupled with parameterisations of the transfer velocity (see for example [Plass-Dulmer et al., 1995](#); [Broadgate et al., 1997](#)).

The main significance of NMHCs from marine sources lies in the disproportionate influence of their emission on the atmospheric chemistry of remote oceanic regions ([Donahue and Prinn, 1990](#); [Carslaw et al., 1999](#)), but for global models to be fully comprehensive we need to account for marine NMHCs from all areas.

* Corresponding author. Plymouth Marine Laboratory, Prospect Place, Plymouth, UK, PL1 3DH, UK.

E-mail address: nigi@pml.ac.uk (N. Gist).

However, NMHC measurements have so far been geographically biased to areas of the Atlantic, Gulf of Mexico and the Caribbean, and little is known at present of coastal versus open-ocean concentrations (Shaw, 2001). Current annual global flux estimates of marine NMHCs are based on the extrapolation of a small number of measurements from limited areas, so they are greatly affected by the specific regionality and seasonality of the measurements, and reflect the particular time and place of sampling rather than a global picture. Pronounced seasonal cycles of NMHC concentrations have been observed previously in UK coastal waters. If such temporal variability occurs in the open ocean, previously calculated annual fluxes for the higher latitudes may have been overestimated by up to an order of magnitude (Broadgate, 1995).

This work presents in situ concentrations of ethene and propene over a full seasonal cycle, in sub-littoral waters, an environment where few measurements have been made of these gases. We focus on ethene and propene because they dominate the oceanic composition and sea–air flux of the NMHCs (Plass-Dulmer et al., 1993). The need for seasonal measurements of NMHCs has been highlighted by a number of studies (see, for example, Bonsang et al., 1990; Plass-Dulmer et al., 1995; Broadgate et al., 1997), since their temporal variability is significant, and this has implications for annual global flux estimates. However, a seasonal study (Broadgate et al., 1997) carried out in North Sea coastal waters was, to our knowledge, the first and only one to monitor the concentrations of ethene and propene in seawater throughout a full seasonal cycle.

This temporal variability highlights the need to predict ocean–atmospheric NMHC fluxes under a range of conditions, but we will need a thorough understanding of the production mechanisms and factors that affect them before this is possible (Ratte et al., 1993). NMHC production mechanisms have been investigated previously in field-based studies (see for example Bonsang et al., 1992, 1993), as well as within the laboratory (see for example Ratte et al., 1998; Riemer et al., 2000), and it is generally accepted that the short-chain alkenes are formed via the photochemical breakdown of DOC in seawater (Ratte et al., 1998; Riemer et al., 2000). A biological influence on short-chain alkene production has long been recognised (Wilson et al., 1970; McKay et al., 1996), but light is also required for significant production to occur (Swinerton, 1974; Bonsang et al., 1993). Light from the UV region induces production of the light alkenes at a higher rate to visible light (Ratte et al., 1998; Riemer et al., 2000), and diurnal cycles of ethene and propene concentrations in marine air were

observed, with maxima at solar noon (Lewis et al., 2001). Dark biological reactions alone do not appear to be directly responsible for the production of hydrocarbons, although they may be involved in the production of their precursor compounds (Riemer et al., 2000). However, macroalgae was recently found to emit a number of NMHCs, including the alkenes studied here, in both light and dark conditions (Broadgate et al., 2004). In the absence of these higher plants, though, it appears that alkenes are primarily formed from the photochemical transformation of DOC.

The in situ data presented here demonstrates that ethene and propene concentrations in seawater exhibit pronounced temporal variability, implying that the factors which affect their production are also heterogeneous. Following previous studies (Ratte et al., 1998; Riemer et al., 2000), we studied the production of ethene and propene under UV irradiation using a discrete body of seawater (over 200 l, 100 times sample volume). We report net production rates of ethene and propene induced by UV irradiation, and results from the study support a photochemical mechanism for NMHC production in seawater.

2. Experimental

2.1. Sampling and analysis

2.1.1. Field-based seasonal study

Seawater was collected between July 2000 and August 2001 from North Yorkshire coastal waters. The sampling site was South Bay, Scarborough, North Yorkshire (54.3°N 0.4°W), except during July and August 2000 when water was sampled further down the coast, at North Landing, Flamborough Head, North Yorkshire (54.1°N 0.1°W). The main sampling site in Scarborough is characterised by fine sediment sand with discreet areas of visible rocks and seaweed, which were easily avoided during collection; the other location, Flamborough Head is a rocky shore cove overlooked by chalk cliffs, which has a much greater abundance of macroalgae. Water was sampled within 50 m of the shore at low tide (depth 1–1.5 m), from within 40 cm of the sea surface by wading. Samples were collected monthly (except in December 2000 when no samples were collected), although sampling frequency was increased (maximum frequency, 4 sampling days in April 2001), during the spring and summer months. Sampling was carried out between 0900 and 1300, and at least 3 replicate samples (collected at the same time but into separate bottles) were analysed for each sampling point. Mean standard error on all replicates was 6% for ethene and 8% for propene.

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