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ScienceDirect
Marine Chemistry 105 (2007) 129–139
MARINE CHEMISTRY
www.elsevier.com/locate/marchem

Net loss rates and distribution of molecular hydrogen (H_2) in mid-latitude coastal waters

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Received 1 August 2006; received in revised form 11 January 2007; accepted 16 January 2007
Available online 26 January 2007

Abstract

We present the first reported net loss-rate constants of molecular hydrogen, H_2, in seawater. Net loss rates and depth profiles of hydrogen were measured in coastal seawater at two mid-latitude sites in eastern Canada: the St. Lawrence Estuary and Halifax Harbour, between November 2005 and July 2006. Net loss-rate constants ranged between 0.29 d^{-1} and 6.07 d^{-1} in the St. Lawrence Estuary, and from 0.14 d^{-1} to 8.67 d^{-1} in Halifax Harbour. The 0.2 μm–5 μm particle size fraction was associated with H_2 loss, implying bacterial consumption. There was a correlation between net loss-rate constants for H_2 and CO suggesting that both substrates shared a common sink. Dissolved hydrogen profiles measured in the St. Lawrence Estuary and Bedford Basin during winter and spring generally showed H_2 levels below atmospheric equilibrium in surface waters and declining with increasing depth. Bedford Basin surface water was supersaturated (125–257%) on sunny days in June and July suggesting that net H_2 production was linked to irradiance, although the exact nature of the source is yet to be determined. A series of light and dark incubation experiments showed lower net H_2 uptake rates in irradiated samples suggesting either H_2 photo production or light inhibition of H_2 uptake.

Keywords: Hydrogen (H_2); Gas chromatography; Degradation; Production; Micro organisms; Carbon monoxide; Canada; Atlantic coast; St. Lawrence; Nova Scotia

1. Introduction

Molecular hydrogen (H_2) is recognised as an indirect greenhouse gas because it influences the concentrations of tropospheric methane and stratospheric water vapour (Ehhalt and Prather, 2001). The global hydrogen cycle is seriously perturbed by human activities, with fossil fuel combustion and biomass burning being the major anthropogenic sources (Novelli et al., 1999). The H_2 tropospheric mixing ratio, currently just above 500 ppbv in the Northern Hemisphere, has shown an upward trend of 0.6% H_2 y^{-1} in the 1980s (Khalil and Rasmussen, 1990) and 0.24% H_2 y^{-1} in the 1990s (Simmonds et al., 2000). Hydrogen is often promoted as an ideal, non-polluting fuel that will eventually become the major energy carrier in a future 'hydrogen economy'. It is however, a highly diffusive gas and there has been some discussion that, in large-scale hydrogen manufacture and transport, leakage will lead to a significant increase

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doi:10.1016/j.marchem.2007.01.009

in the atmospheric H_2 burden (Prather, 2003; Shultz et al., 2003; Tromp et al., 2003).

The role of the ocean in the global hydrogen budget remains poorly understood. Measurements made in low-latitude regions have revealed that H_2 is supersaturated in the surface ocean, and that its concentration declines exponentially with increasing depth below the mixed layer (e.g. Herr et al., 1984; Scranton et al., 1982; Scranton, 1984). In contrast, two studies made in cold high-latitude waters have found H_2 to be generally below atmospheric equilibrium throughout the water column (Herr et al., 1981, 1984). This apparent dichotomy is consistent with ubiquitous marine H_2 consumption, but with a localised source of hydrogen, possibly photobiological, in the near-surface subtropical ocean.

It is likely that marine hydrogen production and consumption are both predominantly microbial processes. Obligate anaerobic, hydrogen-producing bacteria present in low-oxygen microenvironments have been suggested as a source of hydrogen in near-surface seawater (Schropp et al., 1987), and the marine cyanobacterium *Trichodesmium thiebautii* is known to release molecular hydrogen while fixing nitrogen (Scranton et al., 1987). It is probable that at least some hydrogen uptake can be attributed to aerobic hydrogen-oxidising bacteria. One such obligate hydrogenotroph, *Hydrogenovibrio marinus*, was recently isolated from seawater (Nishihara et al., 1989, 1991, 1998, 2001); however, the hydrogen-oxidising microbial community may be taxonomically highly diverse (Friedrich and Schwartz, 1993; Schwartz and Friedrich, 2005).

The ocean is currently thought to be a modest net source of hydrogen estimated at 3 ± 2 Tg y^{-1}, or around 4% of the total global source (Novelli et al., 1999). This flux estimate is highly uncertain and based on very limited spatial data coverage. In the light of an awakening

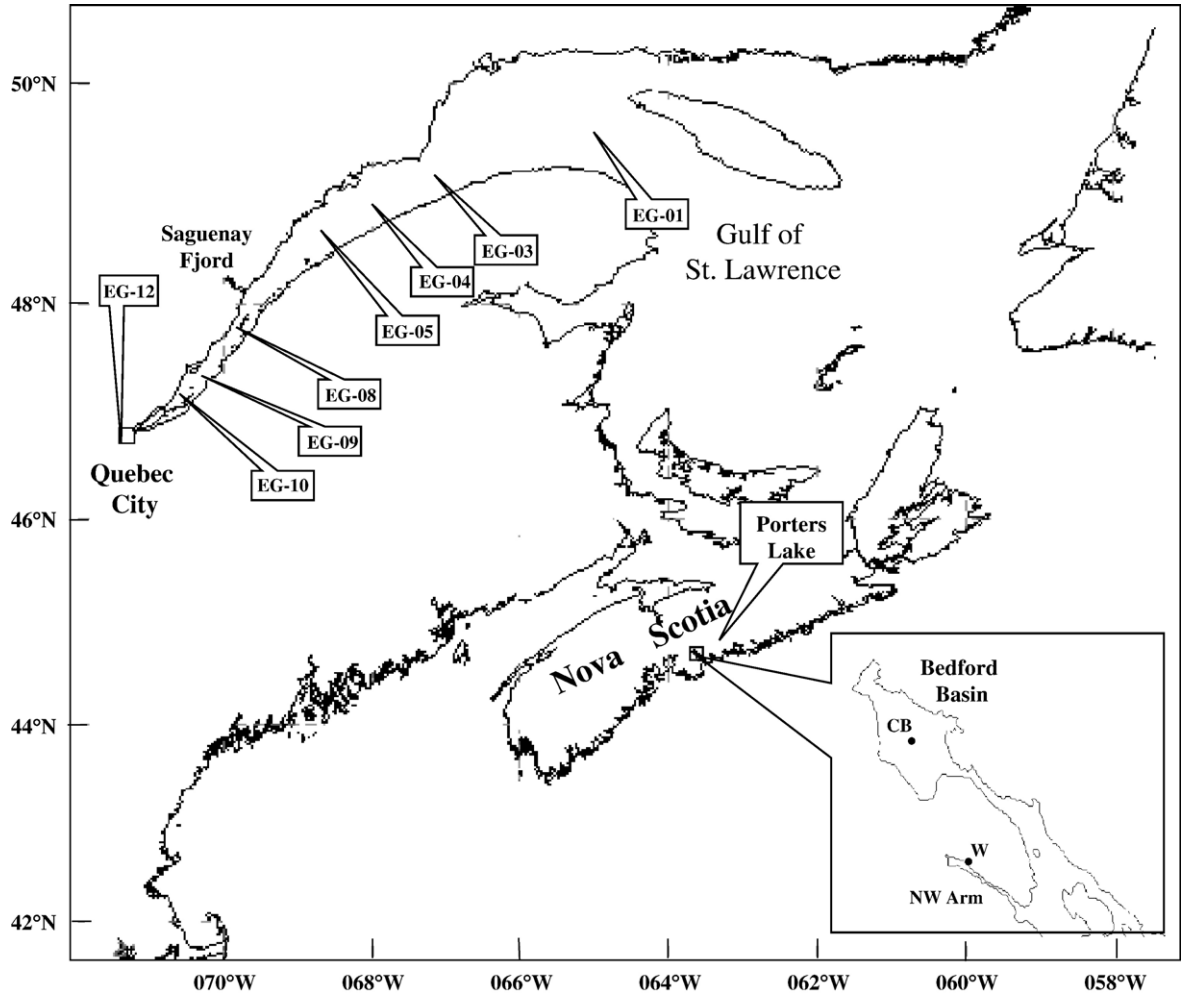

Fig. 1. Locations of the study sites and sampling stations in eastern Canada.