The biogeochemistry of toluene in coastal seawater: radiotracer experiments in controlled ecosystems

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Abstract. The fate of toluene in coastal seawater was investigated in controlled ecosystems using 14C- and 3H-toluene as tracers. Under winter-like conditions, 80% of the toluene volatilized from the water column in 2 months. Microbial degradation was less important than volatilization and sorption onto particulate matter with resultant loss to the sediments was minor. During summer most of the toluene was degraded by microbes. Nearly 80% of the toluene was converted to CO2 within 1 week and the label remained in the water column as dissolved CO2. The experimental results were applied to estimate the removal rates and the residence time of toluene in adjacent Narragansett Bay, Rhode Island. In winter volatilization would dominate the loss of toluene and a residence time of 6 d would be predicted. However, rapid biodegradation in summer would result in a residence time of < 1 d.

Introduction

Toluene is one of the most abundant volatile organic compounds (VOC) in coastal seawater. Concentrations range from several thousands of ng l\(^{-1}\) in Narragansett Bay near Providence, Rhode Island to tens of ng l\(^{-1}\) in waters remote from urban source areas (Schwarzenbach et al. 1978; Sauer et al. 1978; Gschwend 1979; Sauer 1980; Gschwend et al. 1980; Sauer 1981; Gschwend et al. 1982; Wakeham et al. 1983a). Toluene's relatively high solubility in seawater (Sutton and Calder 1975; Rossi and Thomas 1981), its relatively high toxicity to marine organisms (Rise et al. 1977; Hutchinson et al. 1979), and its high concentration in many coastal areas makes it important to understand the environmental fate of this and related compounds. Our previous mesocosm experiments (Wakeham et al. 1983b) suggested that volatilization plays a dominant role in removing toluene from seawater under a range of natural conditions, with biodegradation as an additional sink primarily in summer. However these experiments provided limited information about rates and mass balances could not be calculated. In the experiments reported here, the fate of toluene was studied in a marine mesocosm using 14C- and 3H-toluene as tracers. Time-course changes in activities of dissolved 14C-toluene, 14C incorporated into intermediate metabolites, 14CO2, and 14C associated with particulate matter were
measured. Microbial activity, \(^3\)H-toluene uptake, and \(^{14}\)C-toluene respiration were also examined. With these data, mass balances were calculated which account for most of the \(^{14}\)C-toluene initially added to the ecosystem and allow us to predict the fate and residence time of toluene in Narragansett Bay.

Materials and methods

The MERL (Marine Ecosystems Research Laboratory, University of Rhode Island) mesocosm is a fiberglass tank 5.5 m high and 1.8 m in diameter, containing 13.3 m\(^3\) of Narragansett Bay seawater (Pilson et al. 1977; Santschi 1982). The experiments were run in batch and without sediments. The tank water column was mixed four times a day to simulate tidal turbulence in the bay. Two whole-tank \(^{14}\)C-toluene experiments were conducted.

1. On 24 March 1982 approximately 250 \(\mu\)Ci of [methyl-\(^{14}\)C]-toluene (Amersham Corp., 30 mCi mmol\(^{-1}\)) were added to a tank which had been filled 2 d previously. The spike was prepared by mixing 5 ml of acetone containing the \(^{14}\)C-toluene into 1.5 l of seawater in a 2-l separatory funnel. This solution was then drained through a Teflon tube into the middle of the water column during mixing. Unlabeled (cold) toluene in the spike gave an initial concentration in the tank of about 2 \(\mu\)g l\(^{-1}\). Difluorodichloromethane (Freon 12, F-12) was added to the water column as a gas exchange tracer (see Bopp et al. 1981 for F-12 addition procedure). After the addition, the tank was mixed for several hours before sampling began. The distribution of the label was followed until 20 May 1982. The purpose of this experiment was to simulate cold-water conditions (hereafter termed winter) so the tank was cooled by heat exchangers; nevertheless water temperatures gradually increased from 2 to 10°C.

2. A summer experiment was carried out between 23 August and 19 September 1982, when water temperatures were 18–19 °C. Some 350 \(\mu\)Ci of \(^{14}\)C-toluene (30 mCi mmol\(^{-1}\)), the cold toluene, and F-12 were added as described above to a freshly filled tank.

Water samples were collected through Teflon tubing from 1 m depth during mixing. Samples processed at MERL were analyzed as soon as possible following collection, while samples to be returned to Woods Hole Oceanographic Institution (W.H.O.I.) were collected in glass bottles without headspace, poisoned with HgCl\(_2\), and analyzed within a few days. Samples were stored at 0 °C.

We traced the \(^{14}\)C-activity in several compartments of the mesocosm.

1. Total-\(^{14}\)C. The total \(^{14}\)C-activity in the tank was determined directly by liquid scintillation counting (LSC) at MERL. Duplicate 2.5–1 samples were collected and two 10 ml subsamples from each were pipetted into liquid scintillation vials containing 10 ml of Aquasol scintillation fluor (New England