

Behavior and stability of organic contaminant droplets in aqueous solutions

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Abstract

The behavior of several hydrophobic organic compounds (HOCs) in water at concentrations close to and above their maximum solubility values was studied. For this purpose, solutions of benzene, toluene, xylene, trichloroethylene (TCE) and a mixture of them were prepared in excess in freshwater and in saltwater, and solution stability was examined. High organic concentrations were found to remain stable in both freshwater and saltwater. In saltwater, for example, toluene and xylene concentrations remained as high as 14 and 26 times their solubilities, respectively, over a period of 6 days, while in freshwater, their concentrations remained 8 and 30 times their solubilities over the same period. This phenomenon is attributed to the presence of stable organic droplets, which were observed using optical microscopy. In addition, the transport of HOC droplets through sand is demonstrated, using an experimental system consisting of a saltwater source reservoir connected by a porous inactive sand layer to a freshwater collector reservoir.

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1. Introduction

Many coastal marine environments are highly contaminated by toxic organic pollutants, originating from oil spills, industrial solvents, sewage discharge and other emissions of anthropogenic substances. In this context, it has been shown that immiscible oil components become emulsified and disperse in the water column as small droplets (Delvigne and Sweeney, 1988; Li and Garret, 1998; Tkalich and Chan, 2002; Shaw, 2003). Droplet generation is enhanced by winds, currents and waves, and small droplets can be propelled deep into the water column and be dispersed by the currents. Therefore, the total concentration of organic compounds in natural seawater consists of the dissolved contaminant as well as of mechanically dispersed organic droplets. The actual content of organic pollutants in water may thus be much higher than expected from sol-

ubility considerations only. Dror et al. (2003a) refer to this elevated concentration as the carrying capacity of the aqueous solution (CCAS). Here and throughout, the term CCAS will be used to describe the combined amounts of dissolved HOC, and pure HOC phase suspended in droplet form, within the solution.

The mechanism of droplet formation during vertical mixing of oil floating on the sea surface, for example, is of particular concern, and not fully understood (Tkalich and Chan, 2002). Breaking waves introduce significant energy into the upper ocean layer, with the rate of energy dissipation depending on wave and environmental conditions. During wave breaking, a certain part of the dissipated wave energy is extended to entrain the oil droplets from the oil slick into the water column. Breaking waves develop a mixing layer in the upper part of the water column, and a uniform mixing of oil droplets within this layer can be assumed (Delvigne and Sweeney, 1988; Tkalich and Chan, 2002). Below this mixing layer, the vertical distribution of oil droplets is governed by advection and turbulent diffusion. Droplets can rise to the water surface due to

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buoyancy. It is assumed that larger droplets contribute to oil resurfacing, while droplets smaller than a certain threshold radius (empirically set as 50 μm ; Delvigne and Sweeney, 1988; Proctor et al., 1994) remain trapped in the water column, controlled by turbulent mixing.

Organic compounds are generally less soluble in aqueous salt solutions, such as seawater, than in deionized water (Xie et al., 1997) as a result of the well-known phenomenon called the salting out effect (Setschenow, 1889). Due to this process, HOCs found in polluted marine environments, for example, may concentrate at the interface between seawater and freshwater in coastal aquifers, and then be transported into the groundwater (Dror et al., 2003a). Similar processes may occur at other saline–fresh water interfaces. Intrusion of even minute concentrations of HOCs may seriously reduce quality of such freshwater resources.

In a previous study, Dror et al. (2003a,b) demonstrated in laboratory conditions the transfer of HOCs through an inert sand barrier from an artificial saltwater source into a freshwater collector. Moreover, they found that the concentrations of HOCs in the collector aqueous solutions were in some cases much higher than those expected from solubility considerations. They attributed this to the formation and transport of droplets. Dror et al. (2003a,b) showed that salinity differences produce gradients of chemical activities of the HOCs, which enhance their transport to the less saline side. The processes reducing the aqueous solubility of organic contaminants act to force the contaminants across an interface between two aqueous solutions with varying salinity. This phenomenon was called the salt pump mechanism.

Information on HOC droplet formation, size and persistence in aqueous solutions is limited, with existing studies focusing mainly on surfactant-stabilized emulsions. The paucity of data on average droplet size and distribution is due partly to the difficulty in performing such measurements. Absorption of light transmitted through an emulsion has been used to obtain average interfacial area (McClauglin and Rushton, 1973; Urua and Del Cerro, 1987). The more recent introduction of lasers has enabled development of a number of drop-size measuring techniques, where the amount of light scattered by the drops is related to their size (El-Hamouz and Stewart, 1996; Simmons et al., 2000; Cull et al., 2002). Photography/video recording can provide additional information on the actual shape of the droplets (Pacek et al., 1994; Novales et al., 2003).

Roy-Perreault et al. (2005) showed that stable oil-in-water emulsions for non-aqueous phase liquids (NAPLs) such as polychlorinated biphenyls (PCBs), trichloroethylene (TCE) and diesel fuels are formed in the presence of finely divided solid materials (e.g., bentonite, iron oxide); these are known as Pickering emulsions. Using a stereo microscope they obtained the average droplet size and size distribution of these emulsions. Saleh et al. (2005) showed that TCE-in-water Pickering emulsions with a stability of

greater than 6 months were produced with highly charged polyelectrolyte-grafted silica nanoparticles.

Many questions remain from the various studies discussed above, particularly with regard to the observations of high CCAS without the presence of emulsifiers, and the stability and size of HOC droplets. As a consequence, the objectives of this study were to examine the behavior of HOCs, in both dissolved and droplet forms, in fresh and in saline water. First, the existence of HOC droplets and their stability in aqueous systems was examined by using a combination of gas chromatographic and imaging techniques. The potential for fresh water contamination by HOCs, through droplet transport, was then considered by assessing the transport of HOC droplets through an inert layer of sand.

2. Materials and methods

2.1. Materials and instrumentation

All chemicals were analytical grade and were used as received. Benzene was purchased from Fluka (Germany), toluene and xylene from Frutarom (Israel) and trichloroethylene from Biolab (Israel). Hexane used for extraction was purchased from Sigma (Germany). Inert sand (Unimin, USA; average grain diameter 0.532 mm) used in the barrier was washed with Millipore (18.2 M Ω cm) water prior to experiments. Filters of varying pore sizes were purchased from Acrodisc (0.2 μm , 0.45 μm syringe filters).

The CCASs of HOCs were measured by extracting a sample at a 5:1 ratio using hexane and injecting the extract to a gas chromatograph (HP 5890) equipped with a Chrompack WCOT fused silica CPSIL 5CB column (25 m, 0.25 mm) and a flame-ionization detector (FID) having a detection limit of 1.0 mg/l and a resolution of 1 mg/l (i.e., in this case using 5:1 extraction from 200 $\mu\text{g/l}$ of each aqueous solution). Electrical conductivity of solutions was measured with an EC meter (Horiba Twin Cond B-173, Japan).

Droplet size and morphology were determined using an optical microscope (Olympus, Model BX51) with an attached CCD camera (Olympus DP 12 UCMAD 3) used to photograph the droplets. The resolution of the camera was 1280 \times 1024 pixels. Digital images from the camera were transferred to a computer for analysis; dimensions of the droplets were measured using image analysis software.

2.2. Determination of droplet formation and stability

Excess solutions of 4 ml/l benzene, toluene, xylene and TCE were prepared in freshwater (deionized water) and saltwater (deionized water with 30 g/l NaCl). Solutions consisting of a mixture of the four HOCs (4 ml/l of each HOC) were prepared in the same manner. The solutions were mixed in Teflon-sealed 1000 ml glass flasks, on a vertical shaker (MRC TS-600, Israel) at 170 rpm for 24 h.

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