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# Ecological effects from groundwater contaminated by volatile organic compounds on an urban stream's benthic ecosystem

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While the discharge of groundwater contaminated with volatile organic compounds to surface waters is widely reported, assessments of its ecological threat are rare in the scientific literature, largely being restricted to comparisons of riparian groundwater concentrations to water quality guidelines for protecting aquatic life. Here we investigated potential negative impacts on the benthic community from overlapping petroleum hydrocarbon – chlorinated solvent plumes discharging to an urban stream using in-field ecological assessment methods (targeting both meio- and macrobenthos) over multiple scales. Several lines of evidence were suggestive of detrimental impacts from the plumes, including reduced total abundance and richness of benthic taxa, reduced or enhanced abundances of individual benthic taxa, and an altered benthic community structure. However, the findings were not conclusive, as the evaluation was complicated by substantial small-scale (<20 m) spatial variation in concentrations of many other groundwater contaminants, making it difficult to determine reference areas (i.e., those with similar substrate and chemistry, but lacking exposure to plume compounds) and isolate impacts from a single factor. Furthermore, detections of the wastewater indicator acesulfame also demonstrated the issue of uncertain influences from unmeasured contaminants (e.g., pharmaceuticals). Some of the assessment methods showed greater promise than others (e.g., sampling along a gradient rather than having separate impacted and reference sites), which may provide guidance on future field applications. Overall, the study findings suggest a need for further inquiry into the most appropriate application of ecological and ecotoxicological assessment methods to groundwater-based contamination hazards.

## 1. Introduction

A wide variety of volatile organic compounds (VOCs) may contaminate groundwater, including chlorinated solvents (e.g., trichloroethene (TCE), carbon tetrachloride) and petroleum hydrocarbons, especially BTEX (benzene, toluene, ethyl-benzene, xylenes) compounds. Both types are common contaminants at industrial sites and waste handling facilities, but they can also have a wide range of smaller sources within urban environments. The source VOCs typically occur as a non-aqueous phase liquid (NAPL), which can dissolve to limited degrees into passing groundwater. As a result, these NAPL source zones can be long-lasting and affect large volumes of water, thus, commonly creating long plumes of contaminated groundwater (a few 100 m or more; Wiedemeier et al., 1999).

Groundwater contaminated with VOCs has the potential to affect freshwater aquatic ecosystems where it discharges to surface water bodies, and for long periods of time. There are many direct accounts of chlorinated solvent or petroleum hydrocarbon plumes (even mixed plumes; e.g., Cape Canaveral; Wiedemeier et al., 1999) reaching surface water bodies. Several of these studies provide detailed field measurements of chlorinated solvent plumes discharging to streams (e.g. Conant et al., 2004; Chapman et al., 2007; McKnight et al., 2010, 2012; Weatherill et al., 2014; Lee et al., 2015), wetlands (e.g., Lorah and Olsen, 1999; Lorah et al., 2007) and lakes (e.g., Lendvay et al., 1998a,b), with few similarly-detailed studies available for petroleum hydrocarbon plumes (but for an estuarine river; Westbrook et al., 2005). In addition, more broadly based surveys have also detected VOC plumes, in addition to a wide variety of other contaminants, in urban areas along streams (Roy and Bickerton, 2012), major rivers (Ellis et al., 2007; Ellis and Rivett, 2007; Rivett et al., 2011), and lake shorelines (Roy and Malenica, 2013). Undoubtedly, a myriad more of examples are contained in reports to local regulators.

Lab-based toxicity bioassays have shown that many of the VOCs commonly found in groundwater are toxic to various aquatic organisms. This has allowed development of water quality standards for aquatic life (e.g. Water Quality Guidelines for the Protection of

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Aquatic Life (Canada; CCME, 1999) or Criteria for the Protection of Aquatic Life (United States; US EPA, 2016)). Commonly, estimates of the toxic threat to aquatic organisms from the discharge of contaminants in groundwater have been based on comparing measured groundwater concentrations to these standards (e.g. Conant et al., 2004; Roy and Bickerton, 2012; Roy and Malenica, 2013). Such is the recommended practice for screening level assessments at sites with potentially discharging contaminated groundwater, stipulated in federal guidance documents in the US (US EPA 2008) and Canada (Environment Canada, 2012).

Few studies have attempted to assess directly the impacts of discharging contaminated groundwater on surface water ecosystems, i.e., by using field ecotoxicology measurements. Dickman and Rygiel (1998) noted changes in stream biota from pollution-sensitive to pollution-tolerant species for a small spring-fed creek following the creation up-gradient of a landfill; high levels of several metals were measured in the creek, suggesting groundwater transport of landfill leachate. Williams et al. (2000) assessed the relative abundances of macroinvertebrates across 23 springs around Toronto, ON, in comparison to chloride concentrations; from this work, they developed a biological index for (road salt) chloride impacts. Greenberg et al. (2002) investigated the potential toxicity of pore water associated with river sediments contaminated with primarily chlorobenzenes using in situ exposure chambers. They noted reduced survival of several invertebrate species for chambers half-buried in the sediment and under vertically upward water flow (i.e., upwelling conditions; either groundwater discharge or hyporheic return flow). McKnight et al. (2012) assessed the ecological impact from a chlorinated solvent groundwater plume (and pesticides from agricultural application) using river water samples and kick-sampled benthic macroinvertebrates; plume-VOC concentrations in the receiving stream were apparently too low to cause ecological impacts. And recently, Rasmussen et al. (2016) assessed impacts on stream benthic macroinvertebrates (obtained with a surber sampler) exposed to contaminated groundwater from a chemical factory site with chlorinated solvents and pharmaceutical products. They noted a >50% reduction in the density and diversity of sediment-dwelling organisms in sections receiving contaminated groundwater in comparison to upstream and downstream sites (several km away).

In this study, we investigated whether VOC-contaminated groundwater (in this case, overlapping plumes of chlorinated solvents and petroleum hydrocarbons) discharging to an urban stream was having any discernable detrimental effects on the benthic organisms or the benthic community structure. This study is unique in several respects. First, several sampling methods involving community assessment in relation to the measured contaminant distribution (as by Malard et al. (1996)) were tested, with a focus on optimizing for groundwater-specific influences on sediment-dwelling fauna (as suggested by Rasmussen et al., 2016). Second, several spatial scales were considered, with comparison between different reaches (>50 m apart) in one year and comparison along a spatial gradient of a single, but larger (42 m) reach in the second year. And finally, in this study groundwater was sampled directly and assessed for a wide range of toxic compounds; in the studies noted above, impacts from groundwater contaminants were assessed based on surface water concentrations (and some limited hyporheic samples; Rasmussen et al., 2016) and/or with a limited set of chemical analyses. As a result, this study provides additional insight into the actual risk posed by such contaminated groundwater to stream benthic ecosystems. It also reveals potential limitations and improvements for application of these ecotoxicology methods to discharging groundwater plumes.

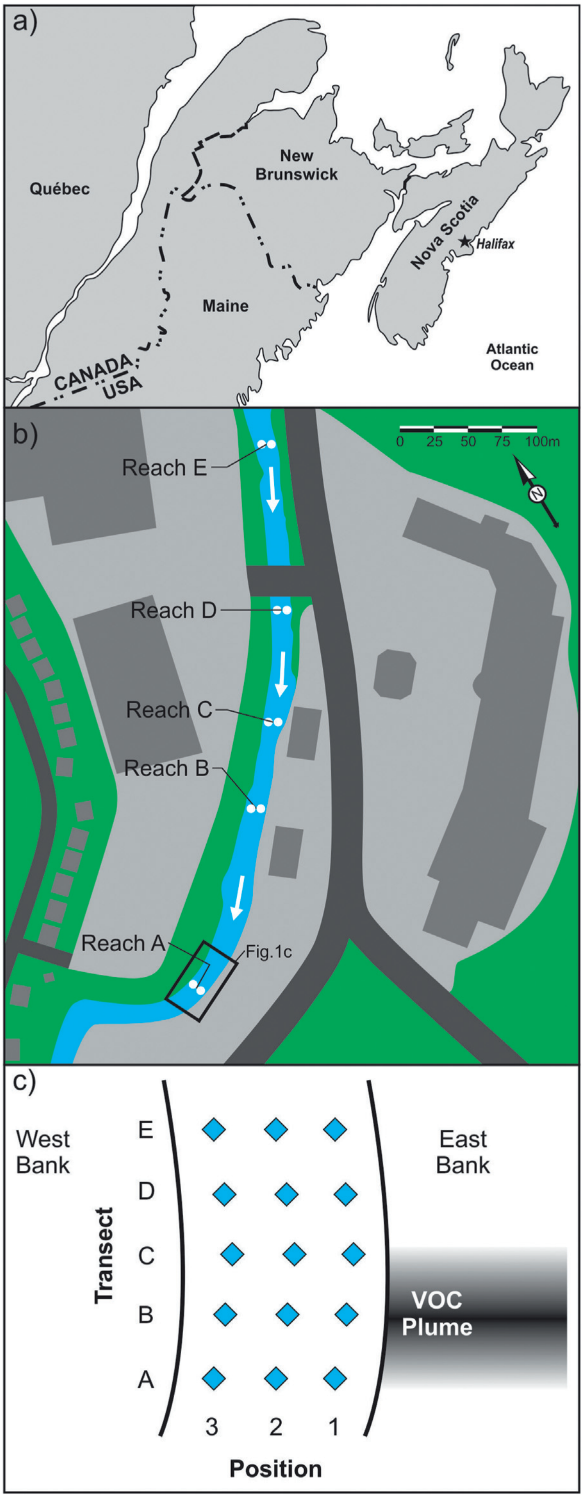

**Fig. 1.** Maps of a) Halifax Regional Municipality (HRM) in eastern Canada, b) stream section for 2010 sampling with the 5 study reaches (A–E), all with east and west sides, and c) stream section for 2011 sampling (area given by box in b), showing the gradient-approach grid (5 transects TA-TE, 42 m; with 3 positions (1–3) across the river width, ~10 m) and zone of the overlapping VOC plumes.

## 2. Study site and approach

This study was performed on a ~350 m length of river (Fig. 1b), which was ~10 m wide and ≤3 m deep, transiting an urban area of the Halifax Regional Municipality (HRM), Nova Scotia (Fig. 1a). Its banks are lined with lawn, pavement, or a narrow strip of trees

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