## Alkylphenols and light aromatic hydrocarbons in oilfield waters are produced in source rocks, not from petroleum hydrolysis

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Diverse experimental, theoretical and empirical evidence has recently been used to suggest that metastable, thermodynamic equilibrium may be attained between oil, water,  $CO_2$  and rock minerals in sedimentary basins. Here, we present evidence which we believe shows that the concentration and distribution of low molecular aromatic hydrocarbons (BTEX: benzene, toluene, ethyl benzene and xylene) and alkylphenols in oilfield waters are not interrelated through redox and hydrolysis reactions. Rather, the concentrations and distributions of BTEX and alkylphenols in oils are inherited from the pattern of compounds generated from kerogen. The distribution of BTEX and alkylphenols in oilfield waters simply represents partition equilibrium between oil and water. The key evidence which favours this simple hypothesis includes:

1. Similar distributions of alkylphenols in source rock extracts and oils

2. Similar distributions of alkylphenols in oils and pyrolysates of source rock kerogen

3. Abundances of alkylphenols and BTEX in oilfield waters which are consistent with partition equilibrium between oil and water, using laboratory measured partition coefficients

4. GC-C-IRMS data which show that phenol in both oil and water is <sup>13</sup>C-enriched by up to 7-8‰ in comparison with coexisting BTEX, which in turn have isotopic compositions which are similar to bulk oil. Bound phenol in source rock kerogen is also significantly isotopically heavier than the corresponding bulk TOC, implying a different source, perhaps carbohydrate or protein moieties.

At least for BTEX and alkylphenols, we suggest that reversible chemical reactions controlled by master geochemical variables such as  $fO_2$  do not appear to be important at the temperatures of most oilfields. Rather, characteristics inherited from the source rock dominate the observed distributions.

## Use of geochemical and isotope tools to evaluate nitrate attenuation in riparian wetlands in agricultural landscape in Southern Ontario

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## Introduction

Nitrate contamination associated with agricultural activities is a major problem in shallow aquifers in Canada and is becoming an increasing threat to groundwater supplies and surface water quality. Riparian zones (buffer strips and wetlands) located at the interface between groundwater-surface water appears to have an inherent ability to naturally attenuate nitrate derived form agricultural sources. The attenuation capacity of riparian zones is linked to a complex interaction between hydrogeological, geochemical and biological conditions. This presentation will focus on research carried out in 5-ha cedar swamp that draines into a lake reservoir. The wetland is fed by nitrate contaminated groundwater originating in upstream agricultural areas. A detailed hydrogeological and geochemical investigation was conducted at the study site.

## **Results and Discussion**

The aquifer is mainly composed of silty sand overlain by organic rich sediments and underlying by clay sediments. However, at a small scale, a significant spatial variability is observed in hydraulic conductivity. The nitrate input in the upstream areas of the wetland range between 16 and 10 mg/L as nitrogen. A significant spatial variability is observed in the nitrate behavior in different parts of the wetland. A general nitrate trend shows a significant drop in concentration to values as low as 1 mg/L along the groundwater flow system toward the lake. Oxygen and dissolved organic carbon concentration patterns suggest that denitrification is the main mechanism responsible for nitrate attenuation at the study site. This is confirmed by  $\delta^{15}N$  and  $\delta^{18}O$  data in nitrate that show the expected trend for denitrification, an enrichment in the isotope composition of the nitrate as the nitrate concentration decreases. The main findings of this study will be compared with other nitrate studies that we have conducted in other riparian zones in Southern Ontario. Our research demonstrate that studies of nitrate attenuation is riparian zones requires a detailed evaluation of the groundwater flow system and groundwater geochemistry.