



# Nitrate addition to groundwater impacted by ethanol-blended fuel accelerates ethanol removal and mitigates the associated metabolic flux dilution and inhibition of BTEX biodegradation



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## ARTICLE INFO

### Article history:

Received 10 June 2014

Received in revised form 13 December 2014

Accepted 15 December 2014

Available online 14 January 2015

### Keywords:

Mixed substrates

BTEX

Fuel ethanol

Metabolic flux

Natural attenuation

GSIM

## ABSTRACT

A comparison of two controlled ethanol-blended fuel releases under monitored natural attenuation (MNA) versus nitrate biostimulation (NB) illustrates the potential benefits of augmenting the electron acceptor pool with nitrate to accelerate ethanol removal and thus mitigate its inhibitory effects on BTEX biodegradation. Groundwater concentrations of ethanol and BTEX were measured 2 m downgradient of the source zones. In both field experiments, initial source-zone BTEX concentrations represented less than 5% of the dissolved total organic carbon (TOC) associated with the release, and measurable BTEX degradation occurred only after the ethanol fraction in the multicomponent substrate mixture decreased sharply. However, ethanol removal was faster in the nitrate amended plot (1.4 years) than under natural attenuation conditions (3.0 years), which led to faster BTEX degradation. This reflects, in part, that an abundant substrate (ethanol) can dilute the metabolic flux of target pollutants (BTEX) whose biodegradation rate eventually increases with its relative abundance after ethanol is preferentially consumed. The fate and transport of ethanol and benzene were accurately simulated in both releases using RT3D with our general substrate interaction module (GSIM) that considers metabolic flux dilution. Since source zone benzene concentrations are relatively low compared to those of ethanol (or its degradation byproduct, acetate), our simulations imply that the initial focus of cleanup efforts (after free-product recovery) should be to stimulate the degradation of ethanol (e.g., by nitrate addition) to decrease its fraction in the mixture and speed up BTEX biodegradation.

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## 1. Introduction

Environmental contamination by single compounds rather than mixtures is uncommon, and microorganisms often face complex mixtures of potential organic substrates. For example,

fuel releases contain a wide variety of compounds, including the relatively water-soluble and toxic BTEX compounds (e.g., benzene, toluene, ethylbenzene and xylenes). Unlike the less soluble hydrocarbons in gasoline that exhibit limited migration potential, BTEX concentrations in impacted groundwater are commonly monitored to assess risk and determine the need for remediation.

Ethanol is increasingly being used as a fuel additive to alleviate dependence on imported oil and greenhouse gas emissions due to fossil fuel combustion (Goldemberg, 2007),

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which increases the likelihood of ethanol-blended fuel releases. Preferential degradation of ethanol and its high electron acceptor demand may decrease the rate of BTEX degradation and increase plume reach (Chen et al., 2008; Corseuil et al., 1998; Da Silva and Alvarez, 2004; Gomez et al., 2008; Mackay et al., 2006; Ruiz-Aguilar et al., 2002; Schaefer et al., 2010).

Although the molecular structure of a compound can significantly influence its susceptibility to degradation (Alvarez and Illman, 2006), the relative biodegradability of a compound in a mixture of alternative substrates (as reflected by degradation rates) is often a concentration-dependent phenomenon (Egli, 1995). Specifically, the relative abundance of alternative substrates in a mixture can significantly influence biodegradation rates of the compound of interest (Bielefeldt and Stensel, 1999; Dou et al., 2008; Freitas et al., 2011; Lendenmann et al., 1996; Lovanh et al., 2002). For example, higher proportions of toluene in various mixtures of toluene and ethanol result in higher toluene biodegradation rates (Lovanh et al., 2002). This phenomenon, termed metabolic flux dilution (Lovanh and Alvarez, 2004), is a form of noncompetitive inhibition of the degradation of a target substrate due to the metabolism of another (likely initiated by different enzymes). This hindrance by alternative substrates in the mixture (e.g., ethanol) can be accounted for by using the metabolic flux dilution factor, which is calculated as the aqueous concentration of a target substrate divided by the total concentration of other dissolved species, expressed as total organic carbon (TOC):

$$f = S_{TOC}/T_{TOC} = r_i/r_0 \quad (1)$$

where  $f$  is the metabolic flux dilution factor (dimensionless),  $S_{TOC}$  is the available concentration of a specific substrate as total organic carbon ( $\text{mg L}^{-1}$ ),  $T_{TOC}$  is the total available organic carbon concentration ( $\text{mg L}^{-1}$ ),  $r_i$  is the degradation rate of compound  $i$  when present in a mixture, and  $r_0$  is its degradation rate when present alone. Thus,  $r_i = f \times r_0$  (Gomez et al., 2008).

Principles and concepts regarding the use of multiple substrates are more easily developed under simple laboratory conditions; however, they have to be validated in real, natural environments. Conditions leading to sequential substrate degradation have different time scales, and therefore, might lead to different observations in the field. In addition, due to differences in the dilution processes, rates of biodegradation and changes in redox conditions, it is very difficult to design laboratory experiments to encompass the complex dynamics of biodegradation in the subsurface. This suggests the need for long-term field studies to determine the effect of ethanol preferential degradation on the attenuation of BTEX compounds.

This study evaluates at the field scale how substrate proportions influence biodegradation of ethanol and BTEX in groundwater, in two controlled release experiments under different redox conditions. Field data are compared with computer simulations using the Modular Three-Dimensional Finite Difference Groundwater Flow (MODFLOW; Harbaugh et al., 2000), Reactive Transport in 3 Dimensions (RT3D; Clement, 1997), and the General Substrate Interactions Module (GSIM; Gomez et al., 2008). These simulations of the dynamics of ethanol and BTEX plumes were used to assess the validity of the metabolic flux dilution model, and to gain

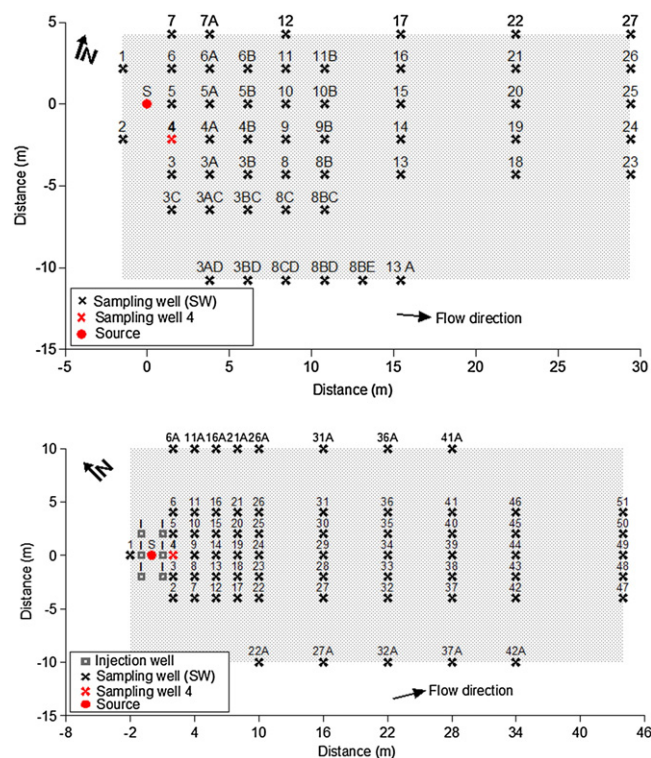


Fig. 1. Schematic view of MNA (A) and NB (B) experimental areas configuration.

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