
Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds

Editors

Bruce C. Alleman
and Andrea Leeson

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CO-SOLVENCY EFFECT IN AQUIFERS CONTAMINATED WITH ETHANOL-AMENDED GASOLINE

Henry Xavier Corseuil (Federal University of Santa Catarina- Brazil)
Marilda Fernandes (Federal University of Santa Catarina – Brazil)

ABSTRACT: This study evaluates the potential effect of ethanol on solubility enhancement of monoaromatic compounds such as benzene, toluene and xylenes (BTX) in aquifers contaminated by ethanol-amended gasoline. The analysis of several ratios of water-gasoline mixtures in equilibrium, corresponding to different ethanol fractions in the aqueous phase, indicates that ethanol enhances aqueous solubility of petroleum hydrocarbons. It was verified that, for ethanol fractions in the aqueous phase of 1% and 10%, BTX mass increases to 3 and 33%, respectively. This effect was greater for xylene (the more hydrophobic BTX compound), followed by toluene and benzene. Simulations carried out with a log-linear model to evaluate the solubility enhancement of petroleum hydrocarbons in the presence of ethanol show that this model is adequate to predict the co-solvency effect. The simplicity of the log-linear equation in representing the co-solvency effect allows this phenomenon to be easily incorporated into contaminant transport models used in risk assessment.

INTRODUCTION

Aquifer contamination caused by gasoline spills from underground storage tanks has been a constant concern worldwide and begins to be discussed with more intensity in Brazil (Corseuil et al., 1996; Corseuil et al., 1998). The gasoline sold in most Brazilian states is a mixture of 78% gasoline and 22% ethanol. The Agência Nacional de Petróleo - ANP (National Agency of Petroleum) changed this mixture to 24% ethanol. Studies have been carried out to evaluate the impact of such mixture to air pollution (Grosjean, et al., 1998). However, despite the great amount of research conducted worldwide on remediation of petroleum hydrocarbon contaminated sites, very little investigation has been done concerning the effects that ethanol-amended gasoline may cause on aquifers. One of these effects is related to a possible enhancement of BTEX solubility in water containing high ethanol concentrations.

The effective water solubility of a particular organic compound present in gasoline or in a mixture of non-aqueous phase liquids (NAPLs) can be estimated from the aqueous solubility of the pure compound and its molar fraction in the gasoline. This solubility will increase if oxygen-containing organic compounds (oxygenates), such as alcohols and ethers, are added to the gasoline. When spilled gasoline comes into contact with water, the existent alcohol in this fuel, being completely miscible in water, will migrate to groundwater. Thus, a high aqueous ethanol concentration can facilitate the transfer of BTEX present in the gasoline to

the aqueous phase, enhancing monoaromatic hydrocarbon solubility in groundwater, a process called "co-solvency effect" (Banerjee & Yalkowsky, 1988). The objective of this study is to evaluate the co-solvency effect of ethanol-amended gasoline in groundwater, and propose a simple mathematical model to predict the possible solubility enhancement of contaminants in the presence of ethanol in groundwater.

Solubility and co-solvency. Solubility is one of the main parameters affecting the distribution/fate and transport of chemical compounds in the environment. According to Raoult's Law, it is possible to calculate the constituent concentration in the aqueous phase, starting from the aqueous solubility of the pure compound and its fraction in gasoline. Due to the presence of oxygenates such as ethanol and MTBE in the gasoline, petroleum hydrocarbon solubility may be potentially enhanced. This solubility enhancement of BTEX and other hydrophobic organic compounds (HOC) in complex mixtures of water and completely miscible organic solvents (CMOS) (denominated co-solvents) has been evaluated by many authors (Banerjee & Yalkowsky, 1988; Pinal, et al. 1990; Poulsen et al., 1992). These studies concluded that HOC aqueous solubility increases log-linearly with the increase of CMOS volume fraction in a mixture of binary solvents. This relationship is expressed mathematically as:

$$\log S_m = \log S_w + \beta f_c \quad (1)$$

where S_m is HOC solubility in the mixture of binary solvents, S_w is HOC solubility in pure water, β is a measure of co-solvency energy, and f_c is the volume fraction of the co-solvent in the mixture of binary solvents. By knowing the values of β for BTX compounds, it is possible to calculate this coefficient for other gasoline constituents (Pinal, et al. 1990):

$$\beta = a \log (K_{ow}) + b \quad (2)$$

where K_{ow} is the octanol/water partition coefficient of COH, and the coefficients a and b are regression parameters applied to a group of hydrophobic organic compounds.

METHODOLOGY

A series of experiments with batch reactors was done to evaluate the effect of BTX solubility in presence of ethanol. The reactors consisted of 60-mL glass vials with Teflon septum and aluminum seal. In these experiments, the co-solvency energy (β) was initially obtained by using pure benzene, toluene, o-xylene and ethanol in an ethanol-distilled water system. Afterwards, co-solvency tests were carried out with ethanol-free gasoline and with Brazilian commercial gasoline (containing 22% ethanol) to evaluate the co-solvency effect and validate the co-solvency log-linear model. The experiments with pure BTX were prepared in triplicate with a water-BTX ratio of 10:1 (experiments done in the presence of one hydrocarbon at a time) with 1.0, 2.2, 4.0, 10.0, 16.0 and 22.0% ethanol. The experiments with ethanol-free gasoline and with the Brazilian commercial gasoline were prepared with gasoline-distilled water ratios of 1:1, 1:2, 1:5, 1:10 and 1:20.

Regarding the Brazilian commercial gasoline, these ratios represented ethanol fractions of 15.8%, 8.47%, 3.62%, 1.81% and 0.93%, respectively. BTX analyses

RESULTS AND DISCUSSION

Figure 1 presents the results of the pure BTX log solubility in relation to the ethanol volume percentage in the aqueous phase. The ethanol-free aqueous solubility for pure benzene, toluene and o-xylene were 1,757, 567 and 202 mg/L, respectively. With the ethanol fraction increase in the aqueous phase, it was possible to observe the increase of BTX solubility. The solubility of BTX compounds in the presence of 10% ethanol exceeded their solubility in pure water 20, 40 and 50% for benzene, toluene and o-xylene, respectively.

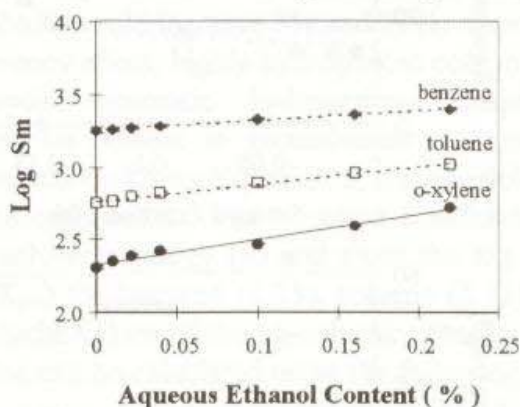


Figure 1. Solute log solubility in a solvent system mixed with ethanol.

Once the co-solvency energy and the aqueous ethanol fraction are known, it is possible to predict, by using the log-linear model, BTX solubility enhancement in water containing ethanol. According to Equation 1, the values of β for benzene, toluene and o-xylene were calculated using the curve slopes of Figure 1, which presents the solute (BTX) log solubility in relation to the ethanol fractions in the mixture. The values obtained for benzene (0.65), toluene (1.27) and o-xylene (1.66) indicate that the co-solvency energy increases according to the greater BTX hydrophobicity. Thus, the more hydrophobic the contaminant, the greater the ethanol effect on solubility enhancement of these compounds.

The experiments with the Brazilian commercial gasoline (ethanol-amended) and with the pure gasoline (ethanol-free) were used to evaluate in which ethanol fraction the co-solvency effect is significant and to validate the co-solvency log-linear model for the Brazilian gasoline. The results with pure gasoline show that BTX solubility remained relatively constant. The average concentration for benzene, toluene and total xylenes in equilibrium in the pure water-gasoline systems were 10.5 mg/L, 28.4 mg/L and 11.7 mg/L, respectively.

The experiment results with the Brazilian commercial gasoline (ethanol-amended) show an enhancement of BTX aqueous concentration along with the enhancement of the co-solvent fraction (Figure 2). Comparing the data between the smallest and the largest ratio of water-gasoline mixture, where the aqueous ethanol fraction ranged from 0.93% to 15.8%, it was observed that the solubility of

The simulations for BTX compounds show that the model presented can be used to predict the solubility enhancement of monoaromatic hydrocarbons in the presence of aqueous phase ethanol. An error analysis for the evaluation of this model, presented in details by Fernandes (1997), indicates that the log-linear model predicts 90% the effect of BTX solubility enhancement, represented by the slopes in Figure 2, due to the increase of the ethanol fraction. However, the exactness of the model, where 100% indicates a perfect estimate, ranged from 105% to 150%. This bigger error is associated with the exact knowledge of the molar fractions of benzene, toluene and xylene present in the gasoline. These fractions will indicate the hydrocarbon solubilities in pure water according to Raoult's Law. For ethanol fractions in groundwater of 1% and 10%, the model predicts that the total BTX mass in the aqueous phase would increase 3% and 33%, respectively.

Because of the co-solvency effect, highly hydrophobic compounds (and hazardous) such as the polycyclic aromatic hydrocarbons (naphthalene, anthracene, phenanthrene, etc) can be present in groundwater contaminated by petroleum hydrocarbon-ethanol mixtures. Using Equation 2, it is possible to determine values of β for other gasoline constituents. The equation coefficients are obtained from the values of the co-solvency energy (β) and from the log of the octanol-water partition coefficient (K_{ow}) for benzene (2.13), toluene (2.73) and o-xylene (3.12) (Howard, 1990). Thus, the values of the co-solvency energy for other constituents of the Brazilian gasoline can be calculated using the following equation:

$$\beta = 1.02 \log (K_{ow}) - 1.52 \quad (3)$$

Based on Equations 1 and 3, and considering a ethanol fraction of 10% in groundwater, it is estimated that the solubility enhancement of naphthalene ($\log K_{ow} = 3.36$) would be 55%. Consequently, besides the enhancement of BTEX mass, the possible enhancement of polycyclic aromatic hydrocarbon concentration in groundwater could increase even more the difficulties associated with remediation of sites contaminated with ethanol-amended gasoline.

CONCLUSIONS

The results indicate that aquifer contamination caused when ethanol-amended gasoline spills come into contact with groundwater will have a greater magnitude than the ones caused by ethanol-free gasoline. This can happen due to the ethanol ability to enhance petroleum hydrocarbon solubility in water. The laboratory experiments show that the increase of total BTX mass is approximately 30% for an aqueous ethanol fraction of 10%. This effect is larger for xylenes which are the less soluble compounds among BTX. As the co-solvency effect is more significant for more hydrophobic gasoline constituents, high ethanol concentrations in aquifer water are likely to facilitate a greater solubility of polycyclic aromatic hydrocarbons which are highly hazardous to human health.

The simulations carried out with the log-linear model to evaluate the solubility enhancement of petroleum hydrocarbons in the presence of ethanol show that this model is adequate to predict the co-solvency effect. The simplicity of the log-linear equation in representing the co-solvency effect allows this

phenomenon to be easily incorporated into the transport models for groundwater contaminants which have been used in risk assessment.

This study indicates that ethanol can be a menace to groundwater because of its ability to enhance the initial concentration of hydrocarbons. In this way, BTEX concentration could be higher in groundwater contamination caused by ethanol-amended gasoline spills than by pure gasoline spills. The possible presence of a large mass of petroleum hydrocarbons and ethanol in the aqueous phase can make the remediation of contaminated aquifers by gasoline and ethanol mixtures even more difficult and costly.

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