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Ethanol induced mobilization of entrapped air in quasi-saturated groundwater systems

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Summary

Groundwater contamination through the transport and storage of gasoline has been of continuous concern in North America as the demand for energy increases. As 8.9 million Canadians rely on potable groundwater for use and consumption, the risk of contamination has significant consequences (Water sources: groundwater, 2013). The understanding of interactions that take place between available aquifer systems and gasoline constituents is crucial for the development of appropriate mitigation and remediation techniques. Biofuels, such as ethanol, are modern constituents being introduced to gasoline in order to improve fuel efficiency and reduce toxic emissions from vehicles (Hill, J., et al. 2009). Despite being introduced as a modern oxygenate additive, the physical and chemical properties of ethanol may result in significant repercussions on available groundwater systems. The objective of this study is to analyze the interactions that take place in quasi-saturated groundwater systems in the presence of ethanol in order to improve the understanding of interactions that take place in available aquifers and modern gasoline oxygenate additives. This research focuses on the unique interactions that occur between ethanol and entrapped gases below the water table. Entrapped gas table can be introduced below the water table through microbial degradation, artificial groundwater recharge, soil swelling, and water table fluctuations. Mobilization of entrapped gases can result in extensive alterations to the natural properties of aquifer systems, such as considerable reductions in hydraulic conductivity, as well as variation in permeability, hydraulic dispersion, and porosity (Marinas, M., et al. 2013). The magnitude of these changes encountered are variable depending on the size and geometry of entrapped air within the system. It is hypothesized that a reduction in interfacial tension (IFT) at the air-water interface of an entrapped air ganglia will induce mobilization, decreasing in size proportional to the reduction in IFT.

Theory / Method / Workflow

Entrapped air is often generated in groundwater systems composed of predominantly coarse sediment surrounding a finer layer boundary. These material boundaries are common in geologic systems that exhibit cross bedding, interbedding, and fractured material. Entrapment of any non-wetting fluid is controlled primarily by the balance of buoyant, viscous, and capillary forces, acting on an immobile ganglion at a critical size and geometry (Pennel, K.D, et al. 1996). The entrapped non-wetting fluid will remain immobile as long as these forces remain in a static equilibrium. An entrapped non-wetting fluid may become mobilized as the buoyant and viscous forces acting on the system exceeds the capillary pressure. In the presence of most chemical surfactants, the capillary pressures at a fluid interface are reduced as a function of its concentration. The chemical and physical characteristics of ethanol, along with other biofuels, contain surfactant properties due to the presence of both a hydrophobic carbon tail and hydrophilic hydroxyl head. Previous models have been developed in the literature to quantify the relationship of the size of an entrapped air ganglion and capillary pressures of the air-water interface (equation 1, Mumford, K. G., et al. 2009):

$$\mathrm{H} = 100\left(\frac{(\mathrm{P_c^{top}} - \mathrm{P_c^{bottom}})}{(\rho_w)\mathrm{g}}\right) \qquad (1)$$

Where H, is the length of the entrapped air pocket, $\mathrm{P_c^{top}}$ is the capillary pressure at the top of the pocket, $\mathrm{P_c^{bottom}}$ is the capillary pressure at the bottom of the pocket, ρ_w is the density of water, and g is the acceleration due to gravity. As capillary pressure is directly dependent on interfacial tension between two fluids, it has been theorized that a decrease in interfacial tension due to contamination of a surfactant will induce a proportional decrease in entrapped air ganglia length.

All experiments were performed in a two-dimensional laboratory flow cell. The cell was packed using a fine silica sand material, surrounded by a coarse background. The cell was packed in an ideal configuration in order to prove the fundamental concept of the direct effects of interfacial tension on entrapped air ganglion size. An entrapped air ganglion was generated below a fine sand entrapment layer by simulating a water table fluctuation event. Ethanol infiltration was established by pooling the alcohol across the cell surface, inducing a constant downwards flux across the cell. Ethanol was continuously introduced to the system for complete contamination of the entrapped air ganglia, simulating a gasoline spill event. Two infiltration events of different flow conditions were conducted on the same packing arrangement to understand the dynamic behaviour of the system. The initial experiments were performed on a low-flow rate system, allowing ethanol to reach the top of an entrapped air pocket prior to the bottom. Consecutive experiments were performed in a fast-flowing system, in which ethanol reached the bottom of the air ganglion, prior to the top.

Results, Observations, Conclusions

Ethanol infiltration in a slow-flow regime exhibited initial ethanol contamination at the upper boundary of the entrapped air pocket. The air was mobilized as the ethanol front reached the upper boundary, in which the rate of air mobilization was observed to decrease non-linearly with time (figure 1). As the ethanol continually infiltrated the flow cell, the entrapped air pocket became contaminated at all interfaces, including the upper and lower boundary of the ganglia. By contaminating all air-water interfaces of the entrapped air system, interfacial tension was reduced from 72mN/m, that of the air water interface, to 23 mN/, that of the ethanol-water interface (Mužíková, Z., et al. 2014). The entrapped air pocket length was observed to decrease proportionally to the decrease in interfacial tension induced, from a length of 7.6 cm to 2.8 cm after establishing 100% ethanol contamination (figure 2).

Increasing the rate of flow in the system by one order of magnitude resulted in unique mobilization behaviour from that observed in the slow-flow regime. Due to the difference in material properties between the fine sand entrapment layer and the coarse sand background. The flow regime of the cell was such that in high flow rate conditions, ethanol would not infiltrate the fine material, but rather surpass the entrapment layer, flowing through the coarse material. Due to the modified flow conditions, ethanol contaminated the bottom boundary of the entrapped air pocket prior to reaching the top, resulting in a unique response to contamination. As the ethanol front reached the lower boundary of the entrapped pocket, a redistribution of air was observed, leading to the appearance of an extended pocket. The pocket increased in length from the initial 7.9 cm to 10.1 cm. This extension was not a result of increased gases to the system, but rather a combination of mass transfer of ethanol to the vapour phase and air redistribution. As ethanol continued to infiltrate the cell overtime, it eventually reached the upper boundary, in which mobilization was initiated. The entrapped air pocket decreased to a final length of 3.9 cm. This decrease in length was proportional to the decrease in interfacial tension, upon applying the theoretical model (equation 1) to the extended pocket.

From this research, it can be concluded that gasoline contamination containing ethanol has the capacity to induce mobilization of entrapped gas in quasi-saturated groundwater systems. The decrease in ganglia size is directly proportional to the decrease in interfacial tension that is induced. This study has emphasized the importance of continuous analysis of surfactants in contaminant spills and will look at the effects of biofuels in future work. From this research, it is recommended that despite the many advantages of biofuels on the reduction of vehicular emissions, the importance of alternative energy sources is crucial. Alternative solutions may also have negative implications on other environmental components and should not be neglected during the research and innovation process.

References

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Figures

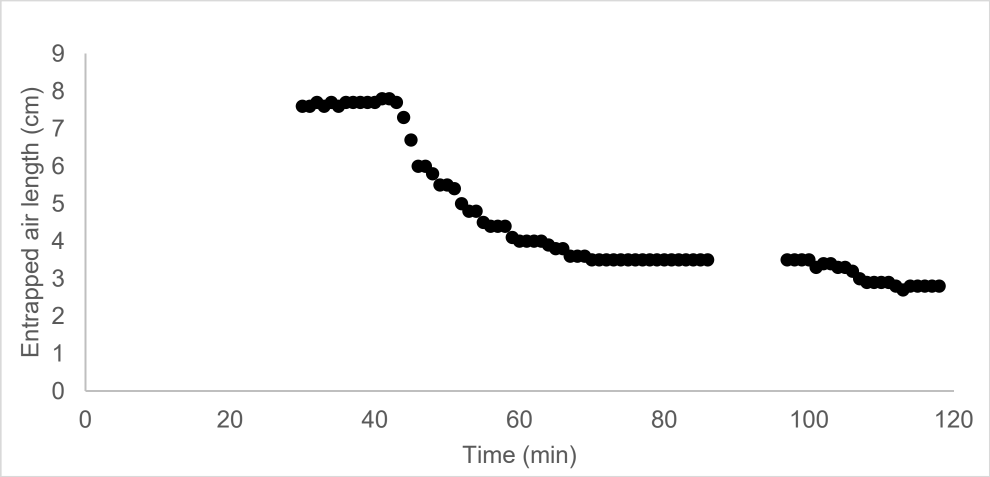

Figure 1. *Entrapped air pocket thickness over time following infiltration of ethanol to sand surface for slow discharge rate.* A continuous decrease in ganglion thickness was observed overtime as the ethanol continued to propagate throughout the system. A decrease in mobilization rate was observed as concentrations increased with time, proportional to the decreases in interfacial tension.

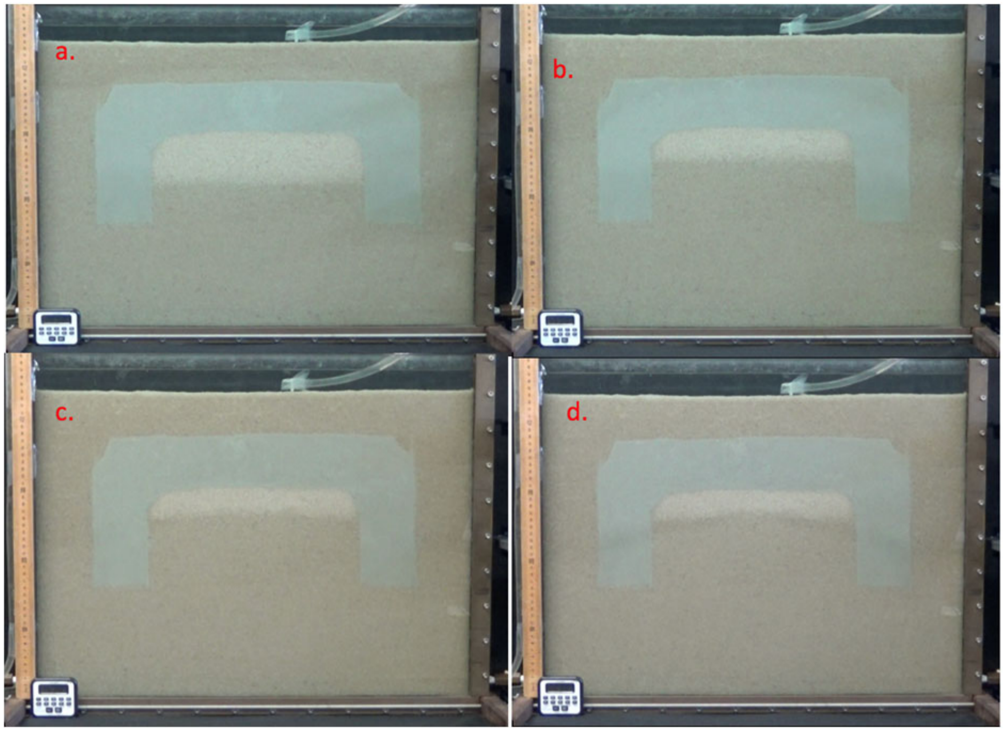

Figure 2. *Mobilization of entrapped air with time during an ethanol infiltration event.* A. system with initial entrapped air ganglion, b. system after 50% air escape, c. system after 31% air escape, d. redistribution of air due to contamination below entrapped pocket, at final entrapped air length.