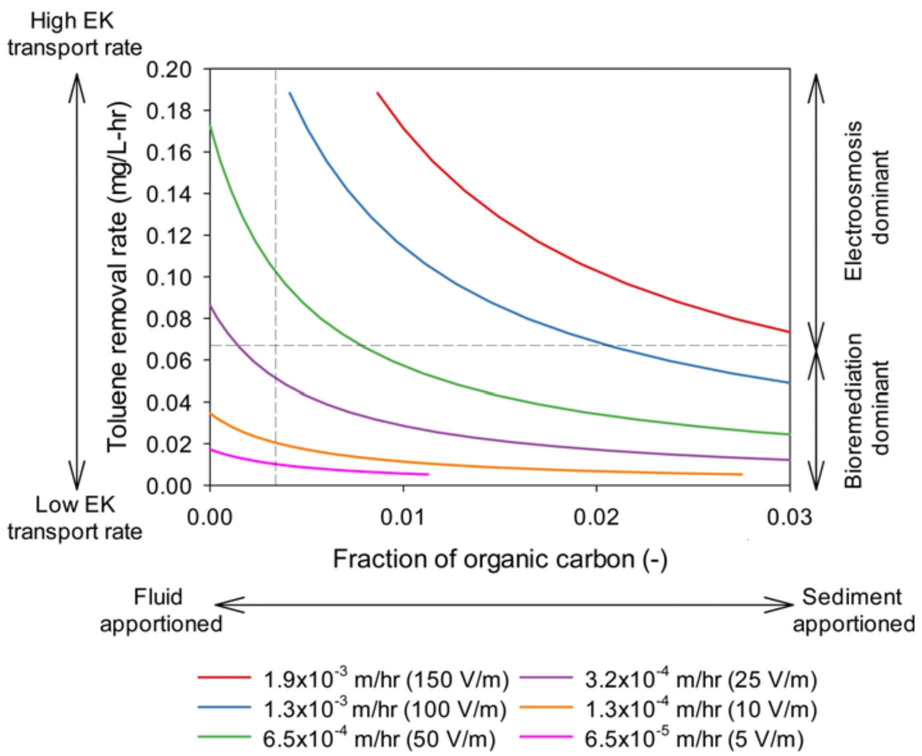

Fig. 8. Sensitivity analysis of toluene removal to different system variables. The different data series represent the toluene removal rate at different electroosmotic flow rates (m h^{-1}) and voltage gradients (V m^{-1}). The dashed lines intercepting the *y*- and *x*-axis represent the toluene removal rate by biodegradation and the experimental f_{OC} value.

factors controlling toluene removal by electroosmosis and to identify the experimental conditions under which stimulating biodegradation would become the dominant toluene removal process in the low-*K* zone. The analysis is shown in Figure 8 where toluene removal rate by electroosmosis is plotted against the sediment f_{OC}. The f_{OC} is back calculated using equations (1)–(5) and the parameters shown in Table 2. The range of f_{OC} values is typical of those observed in the soil or geological environment, <0.01 to 0.03 (Hiscock 2005). The data series represent the toluene removal rate at different electroosmotic pore fluid velocities. These are calculated from equation (1) using the experimental electroosmotic permeability, k_e, value (Table 2) and a range of voltage gradients (1.5–0.5 V m^{-1}). The experimental values for toluene removal by biodegradation and sediment f_{OC} are shown by the dashed lines intercepting the *y*- and *x*-axis respectively. The biodegradation rate is considered at its upper limit because the microcosms were conducted under optimal conditions.

In the context of these experiments the sensitivity analysis shows that the electroosmostic pore fluid velocity must decrease for biodegradation to be the dominant removal mechanism. Within the confines of the experimental parameters already discussed, reduction of the electroosmotic pore fluid velocity is achieved by lowering the voltage gradient. It would need to decrease to *c.* 25 V m^{-1} to generate an electroosmotic pore fluid velocity of 3.2×10^{-4} m h^{-1}, equivalent to a toluene removal rate below 0.066 mg l^{-1} h^{-1}. A low voltage gradient is representative of systems where a constant current is applied and an ionic amendment is added, which will increase the electrical conductivity of the sediment pore fluid (Wu *et al.* 2012*b*). This leads to a decrease in the voltage gradient over time. In these experiments the voltage gradient in Rig D dropped from 72 to 19 V m^{-1} over 91 h of EK application. In addition, the influence of physical heterogeneity may also affect the distribution of the voltage gradient. Gill *et al.* (2015) observed that in physically heterogeneous settings materials with a low effective ionic mobility corresponded to zones with a high voltage gradient. This is shown in Figure 9 for Rig D where the voltage gradient profile (normalized to the voltage between electrodes) is higher across the low-*K* material compared with the high-*K* material. A similar effect was observed in Rig A and Rig C but is less consistent. This effect of heterogeneity could create an enhanced electroosmotic fluid flux across the low-*K* zone, leading to greater contaminant removal compared with homogeneous settings in these experiments.

In the broader context of EK-BIO applications in systems with different properties, a variation in k_e and f_{OC} would change the proportion of contaminant removal by biodegradation and electro-osmosis. First, sediment with a high k_e and subsequent high electroosmotic pore fluid flux is advantageous for contaminant removal but can hinder EK-BIO applications. The k_e in these experiments is 3.7×10^{-9} m^2 V^{-1} s^{-1} (Table 2), similar to values in the EK-BIO literature. For example, Wu *et al.* (2007) and Acar *et al.* (1997) reported k_e values of 2.5×10^{-9} m^2 V^{-1} s^{-1} and 4.6×10^{-9} m^2 V^{-1} s^{-1}, respectively. Second, a high f_{OC} can result in increased retardation that could decrease the toluene transport by electroosmosis below a threshold that makes biodegradation important (in these experiments, 0.066 mg l^{-1} h^{-1}). However, a high sediment f_{OC} can also impede bioremediation, by decreasing the

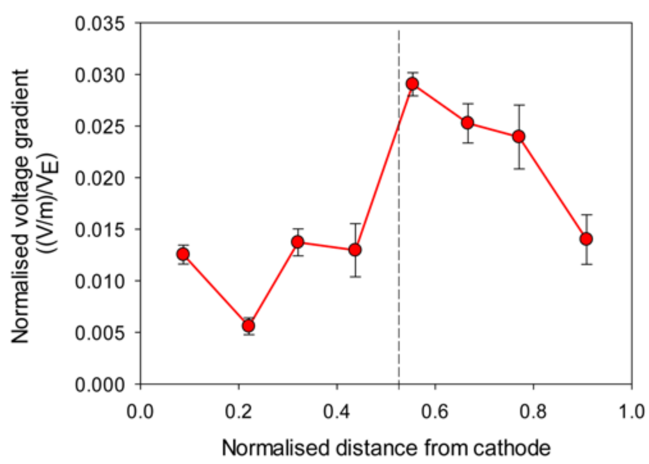

Fig. 9. Voltage gradient across the sediment section normalized to the voltage between electrodes (V_E) for Rig D. Error bars represent one standard deviation from the mean of four time points after the baseline. Dashed line indicates the location of the high-*K*–low-*K* interface.

bioavailability of the contaminant. In these experiments, the reported f_{OC} value 0.0016 allowed electroosmotic removal of 64, 71 and 57% of the toluene mass over 100 h in Rig A, C and D, respectively.

Implications for field applications

These findings indicate that in situations where the contaminant removal rate from a low-*K* zone by electroosmosis is high there will be an increased flux of contaminants into a host high-*K* material. Therefore, in these scenarios it would be more effective to focus bioremediation efforts (e.g. point of amendment addition) within the high-*K* zone. This could be beneficial to the bioremediation process. First, mixing of bacteria, contaminants and electron acceptors by advection and dispersion will be more effective in the high-*K* material. This reduces the mass-transfer limitations on biodegradation of contaminants (Simoni *et al.* 2001). Second, microbial abundance in fine-grained sediments is limited owing to narrow pore sizes (Rebata-Landa and Santamarina 2006). In these settings without the application of EK microbes are less motile and mass transfer is controlled by diffusion. Thus, in high-*K* zones where pore spaces are larger microbes may be in greater abundance and the conditions more conducive to bioremediation. Third, the presence of low-*K* zones facilitates greater mixing in the high-*K* host material, owing to disruption in the advective flowlines down-gradient of the low-*K* zone (Bauer *et al.* 2009).

The method of bioremediation applied within the high-*K* zone could include either natural attenuation or biostimulation. Natural attenuation would be suitable if no immediate intensive remediation action was required and the background supply of electron acceptors in the high-*K* material was sufficient for biodegradation. Alternatively, biostimulation could be applied where electron acceptors or nutrients are introduced to support biodegradation. A similar concept was applied at field scale by Godschalk and Lageman (2005), who developed an EK-biofence to disperse electron donors and limiting nutrients from amendment wells to initiate biodegradation of Perchloroethylene (PCE) downgradient of the contaminant source. If there was a sensitive receptor down-gradient, a hydraulic containment system could be installed to extract the contaminants released into the high-*K* zone. This is similar to the field-scale problem discussed by Gill *et al.* (2016*b*). Typically, the amount of contaminant recovered in these systems decreases over time, but is not necessarily representative of the reduction in contaminant mass still sequestered within the aquifer (USEPA 1994). EK could therefore be used to enhance the extraction of contaminants by hydraulic barrier systems.

Conclusions

This research has important implications for the application of EK-BIO in physically heterogeneous settings. Experimental data show that, under the conditions tested, electroosmosis is the most effective mechanism for contaminant removal from a low-*K* zone compared with diffusion and biodegradation. Further analysis indicated that for biodegradation to become the dominant removal mechanism the controlling parameters for contaminant electroosmotic flow velocity would need to be reduced (i.e. voltage gradient, electroosmotic permeability and sediment f_{OC}). Our initial hypothesis was that EK would enhance *in situ* bioremediation of toluene by increasing the supply of electron acceptors for biodegradation of toluene within a low-*K* zone, in which supply of electron acceptors by advection was poor. This research suggests that EK can indeed enhance *in situ* biodegradation under physically heterogeneous conditions and that a potential driving mechanism could be the electroosmotic movement of toluene out of the low-*K* zone into the high-*K* zone, where *in situ* biodegradation can more readily occur. Overall, this work provides evidence to re-evaluate the mechanism for most effective EK-BIO applications and aids the design of field-based systems that couple EK with bioremediation in physically heterogeneous settings to achieve the greatest *in situ* treatment.

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