# Buffering soil-water acidity in chlorinated solvent bioremediation schemes

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## Abstract
Chlorinated solvents form a significant part of groundwater contamination worldwide. They are difficult to remove via physical means, and anaerobic source-zone remediation based on provision of fermentable e-donor is an attractive clean-up dechlorination option. However, organic acids and HCl lower the groundwater pH and thereby stall the microbial consortia responsible for the biodegradation process. Often, the soil's natural buffering capacity will be exceeded, in which case a strategy of adding buffer to the groundwater is *a priori* beneficial to maintain dechlorination. Geochemical modelling was used to investigate the feasibility of adding naturally occurring buffering minerals to the groundwater for pH control. The simulations revealed that anorthite has the potential to be used as a sustainable pH buffering mineral.

## Key Words
TCE, PCE, e-donor, BUCHLORAC, groundwater alkalinity, kaolinite.

## Introduction
In industrialised countries, more-dense-than-water nonaqueous phase liquids (DNAPLs) are widespread groundwater contaminants. Tetrachloroethene (PCE) and trichloroethene (TCE), both chlorinated solvents, are frequent sources of long-term groundwater contamination (Oolman *et al.* 1995). Anaerobic source-zone bioremediation is an attractive option, with the goal of enhancing the dechlorination sequence (Figure 1): PCE/TCE/DCE (dichloroethenes)/VC (vinyl chloride)/ETH (ethene, harmless).

Aulenta *et al.* (2006) reviewed source-zone remediation research, stating that "in situ anaerobic bioremediation of chlorinated solvents is a cost-effective, expanding technology for the cleanup of chlorinated solvent-contaminated sites. However, this technology is knowledge-intensive and its application requires a thorough understanding of the microbiology, ecology, hydrology and geochemistry of chlorinated solvent-contaminated aquifers". They identified research areas such as small-scale field experiments, experiments with complex water chemistry (as found in the field), effect of transport processes on the e-donor fermentation/dechlorination kinetics, and control of supply of fermentable substrates.

The major microbial processes and associated groundwater chemistry involved in chlorinated solvent degradation are shown in Figure 1, along with a brief explanation of the processes involved. A simple diagram of the source zone remediation concept is shown in Figure 2. This figure illustrates the difficulties with source zone schemes. Placement and timing of e-donor supply, buffer and bioaugmented microbial communities impacts on the scheme viability due to inefficient mixing. Below, the question of the overall buffer requirement is addressed by modelling of the geochemical processes involved (Figure 1), but the complex flow and transport processes to optimize the delivery of this buffer are not considered (Figure 2).

*Buffer requirement, timing and placement*
While dechlorination of TCE to cis-dichloroethene (cis-DCE) will often proceed with pH in the 5-6 range, microorganisms responsible for the further dechlorination of cis-DCE are inhibited at this low pH. So, sustained source zone dechlorination has the potential to overwhelm even reasonably well buffered systems. Where the natural buffering capacity is low, or excessive pH drops are observed, a buffering agent such as sodium bicarbonate is typically added to raise and/or neutralize the pH to ensure sustained dechlorination. McCarty *et al.* (2007) calculated the extent of dechlorination likely to occur prior to pH inhibition for a range of donors and initial groundwater alkalinity. They demonstrated that buffer amendment is likely required for the effective continuation of TCE degradation in DNAPL source areas. Their investigation raised a number of important questions including: the amount of buffering agent required to maintain the pH at a suitable level for dehalogenating bacteria, the influence of mineralogy on the soil's natural buffering capacity, and the influence of competitive $H_2$-consuming side reactions on the level of acidity generated. Robinson *et al.*
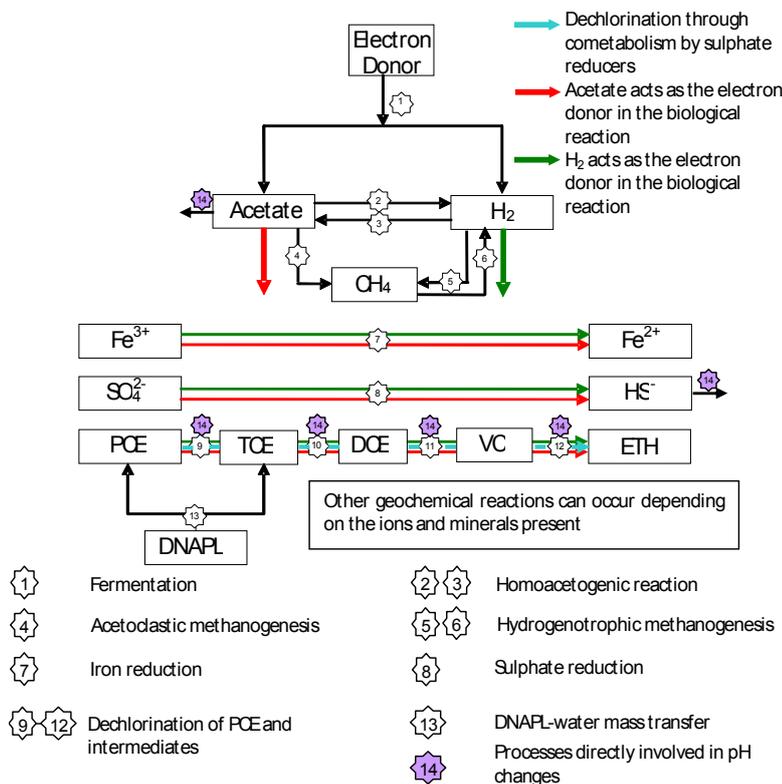
**Figure 1. PCE and TCE degrade anaerobically, acting as electron acceptors, and thus require an organic substrate as an e-donor (electron donor). Fermentation of the latter provides $H_2$ as the e-donor. Electron acceptors such as iron and sulphate compete for $H_2$, reducing the amount available for dechlorination. Rapid dechlorination leads to groundwater acidification and microbial inhibition (Holliger *et al.* 1993; Zhuang and Pavlostathis 1995; Bhatt *et al.* 2007).**
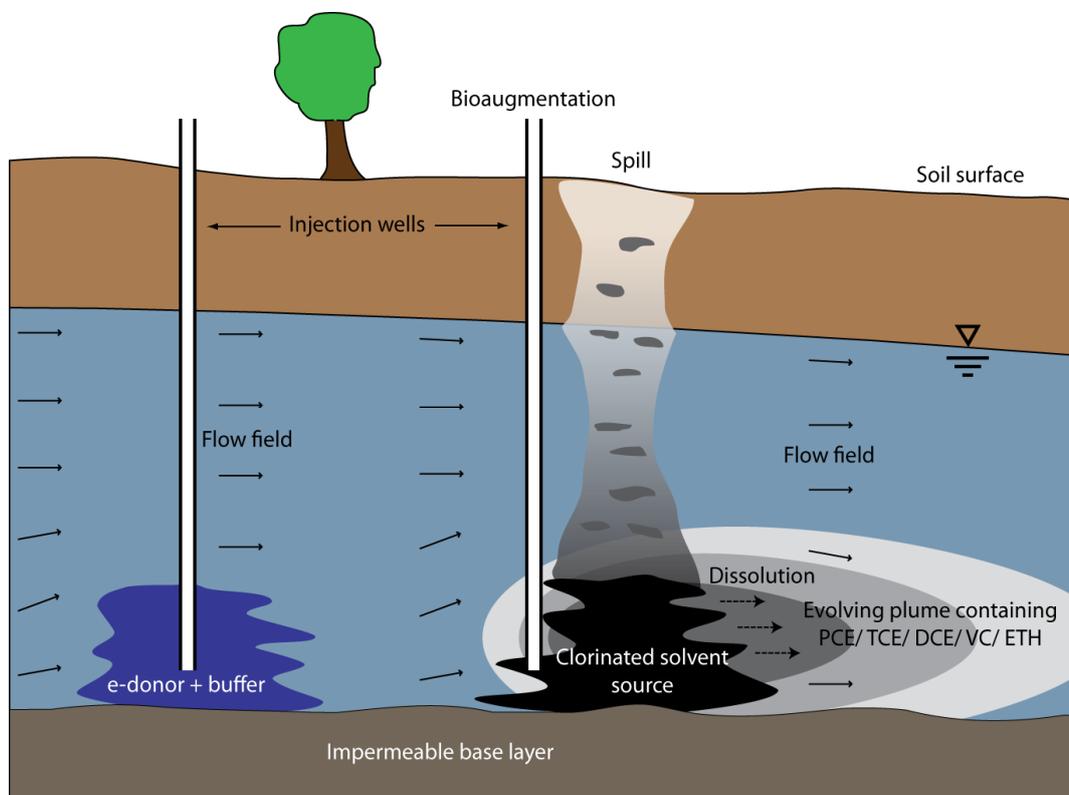


**Figure 2. A source-zone remediation scheme. Chlorinated solvent is spilled or otherwise discharged into the groundwater, its spreading affected strongly by local porous medium properties, forming a long-term contamination source. Source zone remediation involves up-gradient e-donor addition and bioaugmentation with dehalorespiring bacteria.**

(2009) and Robinson and Barry (2009) developed and tested a batch model (BUCHLORAC) to predict the quantity of buffer required as dechlorination proceeds. This model, used below, accounts for site mineralogy and water chemistry, amount of dechlorination and e-donor type.

**Passive buffering using silicate minerals**
Laboratory evidence (Adamson *et al.* 2003) shows that natural soils do not provide the buffering capacity to neutralise acidity produced by enhanced source-zone dechlorination. An alternative strategy is the addition of ground soil minerals to the e-donor emulsion as a built-in buffer. As the e-donor is utilised, buffer will be released to the aquifer to counter the dechlorination acidity, with the rate of release dependent on the mineral used and its particle size. The first question is the choice of soil minerals. Calcite, although very common, is unsuitable. Independent of available surface area and hence overall dissolution kinetics, it does not provide sufficient buffering due to solubility constraints (Robinson *et al.* 2009).

Silicate minerals are also common buffering minerals. However, while they can provide significant pH buffering they are typically slow to dissolve. Simulations (not shown) predict that under natural (no size control via mineral grinding) conditions these minerals cannot provide sufficient buffering on the timescales associated with TCE degradation due to their slow dissolution kinetics. In the following, estimates of relative surface area (surface area mineral/unit volume soil) to achieve the required buffering are presented.

The general rate law for the dissolution for the silicate minerals is (Appelo and Postma 2005):

$$R = k \frac{A_0}{V} \left( \frac{m_s}{m_0} \right)^n g(C) \tag{1}$$

Equation (1) shows that as the overall rate ($R$) depends on the ratio of surface area ($A_0$) over the volume of water ($V$) it is possible to reduce the particle size of the silicate minerals to increase their dissolution rate and thus buffering ability. Simulations (Figure 3) were performed for a soil containing calcite and ground anorthite (Ca-feldspar) as the active buffering mineral. Anorthite dissolves about 700 times faster than the other common silicate minerals K-feldspar and albite (Appelo and Postma 2005), and so has the greatest potential to provide the required buffering. Dissolution of anorthite leads to the precipitation of kaolinite, a process that is included in the model.
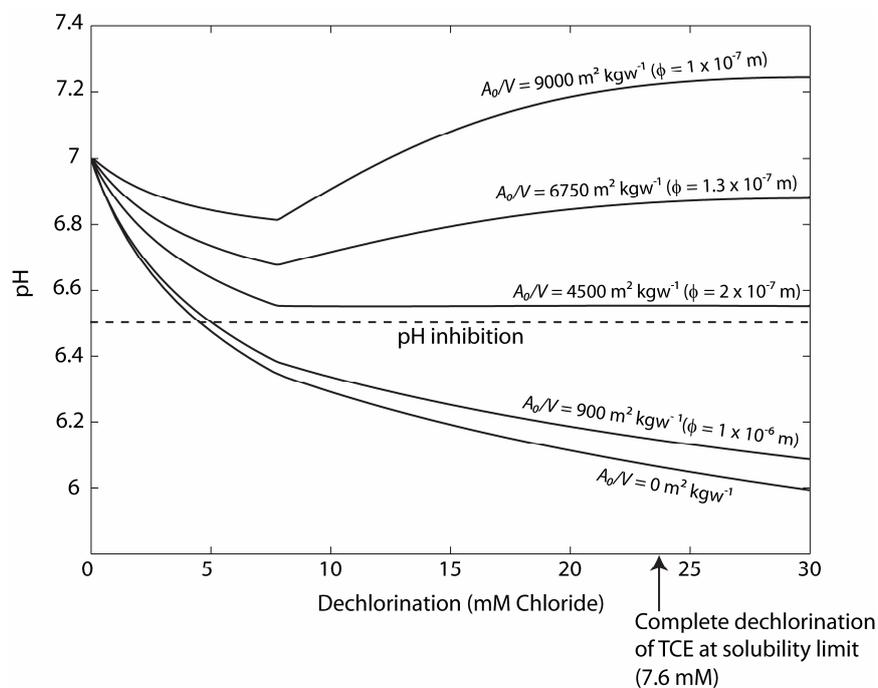


**Figure 3. Effect of extent of dechlorination on solution pH for different surface areas per kg of soil water ($A_0/V$, m²/kgw) and corresponding particle sizes for anorthite spheres ($\phi$) predicted by the model of Robinson *et al.* (2009). The dechlorination rate was estimated from microcosm experiments spiked with 800 mg/L TCE. Linoleic acid is the e-donor, 20% of the $H_2$ generated from e-donor fermentation is used for dechlorination, calcite is present in excess, anorthite contributes 4.2% of the soil weight, porosity = 0.4, soil density = 2650 kg m⁻³, initial alkalinity = 5 meq /kgw, $SO_4^{2-}$ concentration = 7.8 mM.**

## Conclusions

The simulation results in Figure 3 demonstrate that:

- When only calcite is present ($A_0/V$ = 0 m$^2$ /kgw) the pH drops to 5.99 for 30 mM Cl$^-$ produced. Complete dechlorination of TCE at its solubility limit corresponds to 24 mM Cl$^-$ produced.
- If anorthite and calcite are present in their natural state (anorthite as 0.1 mm spheres; $A_0/V$ = 0.9 m$^2$ /kgw), the pH reduces to 6 with $10^{-4}$ mmol /kgw of anorthite dissolved for 30 mM Cl$^-$ produced (not plotted). Due to the low dissolution rate, this is similar to there being no anorthite present.
- As the particle size of anorthite is reduced, its dissolution rate increases and it acts as an effective buffering agent. Figure 3 shows that an anorthite particle size of $1.3 \times 10^{-7}$ m (small!) leads to the optimal dissolution rate for pH control, with $3.1 \times 10^{-2}$ mmol /kgw of anorthite dissolving for 30 mM Cl$^-$ produced. The groundwater pH is highly sensitive to particle sizes of around $10^{-7}$ m.
- The pH response to dechlorination changes after 7.8 mM Cl$^-$ is produced. This results from SO$_4^{2-}$ being depleted, at which time all of the H$_2$ generated from fermentation is used for dechlorination. Then, less acetic acid is formed and less acidity is produced. For particle sizes of $10^{-7}$ m and $1.3 \times 10^{-7}$ m, this results in the pH increasing as the rate at which alkalinity is added to the solution from anorthite dissolution exceeds the rate at the acidity is generated from dechlorination (and donor fermentation).
- If the particle size for anorthite is too small ($< 10^{-7}$ m), dissolution is too rapid and the groundwater becomes alkaline, inhibiting the microorganism activity. The optimal particle size depends on the field conditions and remediation scheme to be implemented. A possibility is to use a consortium of silicate minerals with a range of dissolution rates (including K-feldspar, albite) to achieve more stable pH control.

These results suggest that pH control engineering remediation schemes can be achieved, although several practical issues still need investigating, such as the feasibility of achieving very small ground mineral sizes.

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