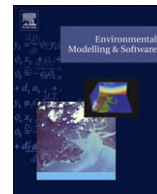




Contents lists available at ScienceDirect

Environmental Modelling & Software

journal homepage: www.elsevier.com/locate/envsoft

Short communication

Design tool for estimation of buffer requirement for enhanced reductive dechlorination of chlorinated solvents in groundwater

Clare Robinson^{*,1}, D.A. Barry

Laboratoire de technologie écologique, Institut d'ingénierie de l'environnement, Station No. 2, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

ARTICLE INFO

Article history:

Received 19 September 2008
 Received in revised form
 21 March 2009
 Accepted 23 March 2009
 Available online xxx

Keywords:

Alkalinity
 Bicarbonate
 Dechlorination
 Dehalogenation
 PHREEQC
 BUCHLORAC
 TCE
 PCE
 Contaminated aquifer
 Remediation
 DNAPL

ABSTRACT

To assist in the design of enhanced reductive dechlorination systems for in situ remediation of chlorinated solvent source zones, the software BUCHLORAC (Buffering of deCHLORination ACidity) was developed to predict the amount of buffer required to maintain the groundwater pH in a DNAPL treatment zone within the optimal range for dechlorinating bacteria. Reductive dechlorination is an acid-forming process with hydrochloric acid and organic acids typically building up in the treatment zone. Remediation of source zones is associated with such extensive localized dechlorination that it may be common for the soils' natural buffering capacity to be exceeded. As groundwater acidification may inhibit the activity of dechlorinating microorganisms and thus slow or stall the remediation process, sufficient alkalinity must be present to maintain a near-neutral pH. BUCHLORAC is a Windows Graphical Interface based on an abiotic geochemical model that is implemented through the program PHREEQC. BUCHLORAC allows users to estimate the buffer requirements for their specific operating and design conditions including, for example, site water chemistry, mineralogy, amount of chlorinated solvent to be degraded, design inhibition pH, and type of organic substrate and buffering additive.

© 2009 Elsevier Ltd. All rights reserved.

Software Availability

Software title: BUCHLORAC
 Developers: Clare Robinson, D. A. Barry
 Contact Address: Laboratoire de technologie écologique, Institut d'ingénierie de l'environnement, Station No. 2, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland. E-mails: clare.robinson@epfl.ch, andrew.barry@epfl.ch, barry@epfl.ch
 Software required: Java Runtime Environment 6.0, Windows 2000/XP/Vista
 Availability: Supplementary material (free to use)

1. Introduction

Chlorinated solvents, such as tetrachloroethene (PCE) and trichloroethene (TCE), are widespread contaminants due to their extensive use, accidental release, and improper disposal over the last century (National Research Council, 2004). They are amongst the most hazardous groundwater contaminants, and in addition, because they are often present in the subsurface as dense nonaqueous phase liquids (DNAPLs), they are also amongst the most persistent (National Research Council, 2004; Rivett et al., 2005). Reductive bioremediation is now recognized as a promising cost-effective technology for the in situ clean-up of chlorinated solvent source areas (McCarty, 1997; Ellis et al., 2000; Major et al., 2002; Yang and McCarty, 2002; Adamson et al., 2003). In recent years increased understanding of dechlorinating microorganisms and the selection of suitable fermentable organic substrates has led to more rapid dechlorination rates and considerably improved the extent of degradation of PCE and TCE to lesser chlorinated compounds. Nevertheless, in spite of these advancements, complete remediation is still often hindered at many sites due to the development of unfavorable aquifer conditions, in particular

* Corresponding author. Tel.: +41 21 693 2757; fax: +41 21 693 5670.
 E-mail addresses: clare.robinson@epfl.ch (C. Robinson), andrew.barry@epfl.ch (D.A. Barry).

¹ Present address: Department of Civil and Environmental Engineering, University of Western Ontario, London N6A 5B9, Canada.

low groundwater pH, which inhibits the activity of the dechlorinating microorganisms (Carr and Hughes, 1998; Aulenta et al., 2006).

The major processes influencing the amount of acidity generated in the DNAPL treatment zone during enhanced reductive dechlorination have been investigated by Robinson et al. (in press). A summary of these processes is provided in Table 1. Reductive dechlorination is a step-wise process with PCE converted to TCE to dichloroethene (DCE) to vinyl chloride (VC), and finally to ethene. Each step involves the addition of electron donor (hydrogen, H₂) and production of hydrochloric acid (HCl). The reduction of R-Cl, a generic chlorinated ethene compound, is given by:



Different organic substrates can be used to provide H₂, with each producing different amounts of organic acids, carbonate species and, in some cases sodium, upon fermentation. For example, the fermentation reaction for linoelic acid (C₁₈H₃₂O₂), the main constituent of water-insoluble substrates such as emulsified vegetable oil is:



Dechlorinating microorganisms must compete for the H₂ produced from fermentation with microorganisms associated with the reduction of non-chlorinated electron acceptors (e.g., sulfate, iron(III)). These competing non-chlorinated reduction reactions not only increase the organic substrate demand but also significantly influence the amount of acidity produced (McCarty et al., 2007; Robinson et al., in press). To ensure effective dechlorination it is necessary to consider the soil's buffering capacity to determine whether there is adequate natural alkalinity available to control the acidity generated. Where the natural buffering is likely to be exceeded, a pH control system may be necessary. This typically involves the addition of a buffer such as potassium or sodium bicarbonate (KHCO₃, NaHCO₃). Groundwater pH is strongly controlled by the dissolved carbonate equilibria and the addition of bicarbonate offsets the impact of the higher dissolved CO₂ concentrations and therefore neutralizes the pH. With recent studies demonstrating that significant acidification of the source zone may occur even in relatively well buffered soils (Adamson et al., 2004; McCarty et al., 2007; Robinson et al., in press), buffer

Table 1
Main factors influencing groundwater acidity during enhanced reductive dechlorination (arrows indicate the direction of pH change).

Process	Influence
Dechlorination	pH ↓
Fermentation	Depends on fermentation products of organic substrate used: Acetate species – pH ↓ Carbonate species – pH ↓ Sodium ion – pH ↑
Sulfate reduction	Direct effect is pH ↑ Overall effect including supply of additional H ₂ depends on organic substrate used
Iron(III) oxide reduction	pH ↑
Acetate fermentation	pH ↑
Calcite dissolution	pH ↑
Iron sulfide precipitation	Direct effect is pH ↓ Overall effect including iron(III) oxide and sulfate reduction depends on organic substrate used
Release of CO ₂ (g)	pH ↑

dosage systems may be a crucial element in the design of a successful remediation strategy.

As a design tool, we have developed BUCHLORAC; an easy-to-use software package that allows a user to predict the acidity generated during dechlorination and the associated buffer requirements for their specific operating and design conditions. Below we describe the features available in BUCHLORAC. The software can be applied to a wide range of field conditions and accounts for the:

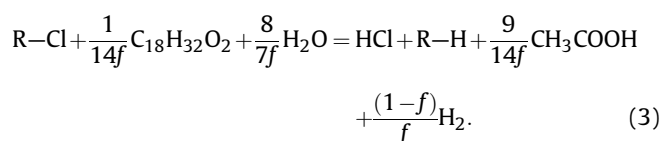
- expected extent of dechlorination,
- site water chemistry,
- fermentable organic substrate added to the groundwater,
- availability of non-chlorinated electron acceptors,
- use of acetate produced from fermentation as a direct electron donor,
- potential for gas release,
- soil mineralogy, and
- complex aqueous speciation.

To demonstrate application of BUCHLORAC an example is presented where the software is used to estimate the buffer requirement for a contaminated chlorinated solvent site. At this site limited dechlorination rates have previously been observed mainly due to acidic groundwater conditions.

2. Description of BUCHLORAC

BUCHLORAC is a Windows Graphical User Interface developed in the Java programming language. The software is based on an abiotic batch (zero-dimensional) geochemical model that is implemented through the program PHREEQC version 2.15 (Parkhurst and Appelo, 1999). PHREEQC performs the chemical reaction and speciation calculations. BUCHLORAC facilitates the creation of a PHREEQC input file, execution of the model and easy visualization of the results. The geochemical model including theoretical background associated with its development is detailed in Robinson et al. (in press), and is briefly described here. In addition, help documentation is available within BUCHLORAC that provides further details of the software's features.

The calculations performed to predict the acidity generated and associated buffer requirements as dechlorination proceeds are outlined in Fig. 1. As the purpose of the model is to simulate the processes influencing the groundwater acidity, the model is abiotic and the complex microbial processes associated with enhanced reductive dechlorination are not simulated directly. Nonetheless, the fraction of H₂ produced from fermentation that is used for dechlorination, rather than for the reduction of non-chlorinated electron acceptors, depends on the activity of microbial populations. As this fraction (*f*) cannot be predicted based on standard thermodynamic considerations, the model assumes that, as a lower bound, a minimum fraction (*f*_{min}) of the H₂ produced is directed to dechlorination, with remainder (1 – *f*_{min}) consumed by competing microorganisms (e.g., sulfate and iron(III) reducers). Of course, if there is insufficient sulfate and iron(III) available, the H₂ produced from fermentation is used for dechlorination. For arbitrary *f*, (1) and (2) are combined to give an overall dechlorination stoichiometry (e.g., for linoelic acid):



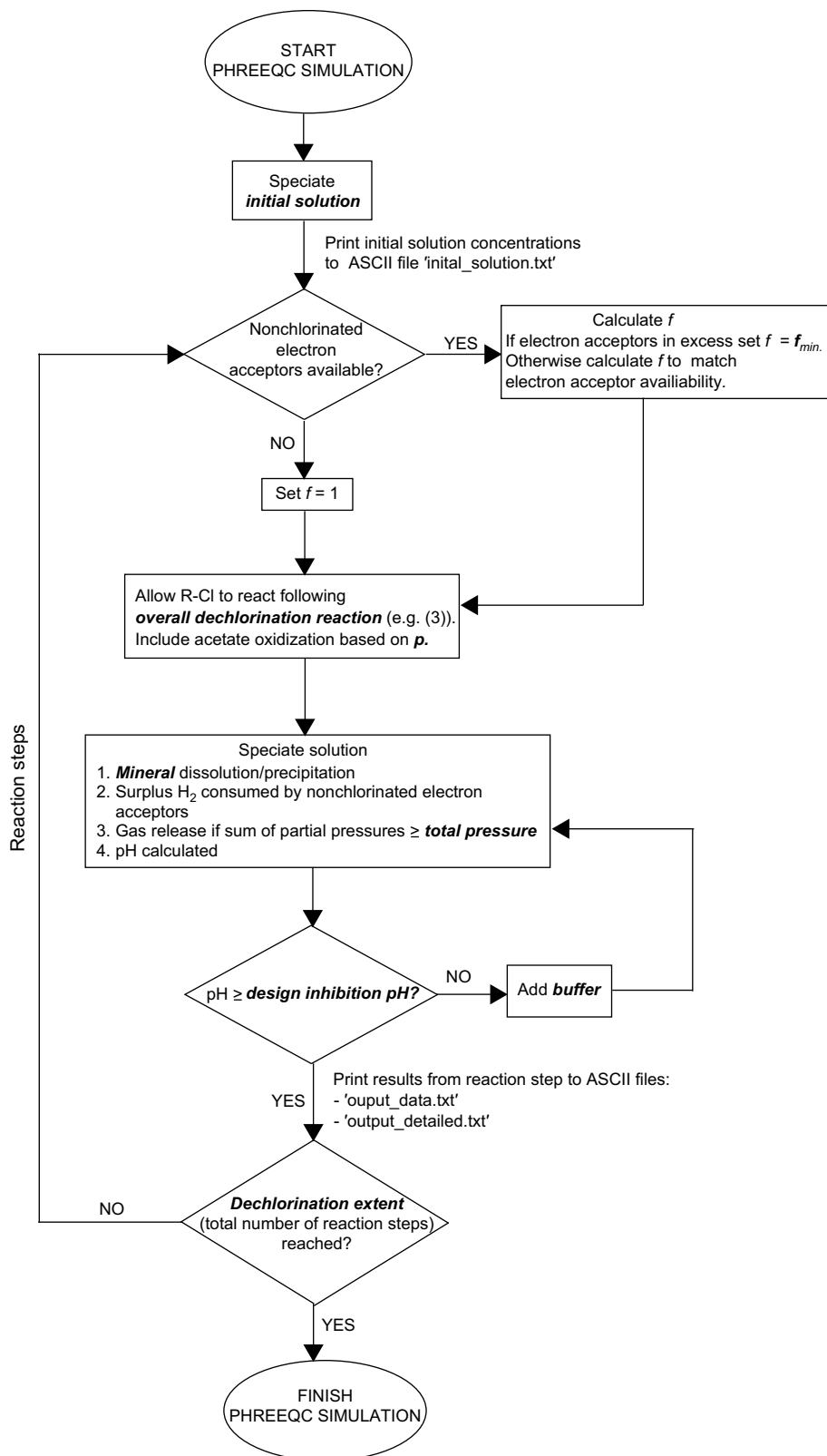


Fig. 1. Flow chart of the PHREEQC model algorithm that performs the calculations within BUCHLORAC. Bold italic text indicates parameters that are specified by the user through BUCHLORAC. A description of the algorithm is provided in Section 2.

Overall reactions for different organic substrates considered in BUCHLORAC are provided in its Help documentation as well as Robinson et al. (in press). The modeling approach is to assume a given amount of R-Cl degrades and to follow this overall reaction

in steps. The solution is speciated at the end of each reaction step and in doing so the surplus H₂ produced in (3) is consumed by the available non-chlorinated electron acceptors. Other reactions affecting the solution chemistry also occur: minerals are allowed to

dissolve and/or precipitate and gas is released if the sum of the partial pressures of all dissolved gases present exceeds a specified total pressure. To perform these calculations PHREEQC uses a geochemical database that contains thermodynamic data for aqueous species, and gas and mineral phases. The database is that used with MINTEQA2 (Allison et al., 1990) with the inclusion of mineral dissolution/precipitation kinetics. When the availability of non-chlorinated electron acceptors is limited, f is automatically adjusted such that only the H_2 required to reduce the available competing electron acceptors is produced in (3). The main task of the program occurs when the pH drops to the user-specified minimum value, following which the program calculates the amount of buffer needed to maintain this pH.

3. BUCHLORAC features

3.1. Input parameters

The user options available in BUCHLORAC are based on extensive use of the geochemical model and thus our understanding of the main factors influencing the buffer requirements (Table 1, Robinson et al., in press). Default parameter values are provided in BUCHLORAC that can be used when values pertaining to the user's specific operating conditions are unknown.

3.1.1. Initial water chemistry

The user is able to specify their influent (background) groundwater chemistry, including concentrations of major cations and anions, alkalinity, pH and temperature (e.g., Fig. 2). Here the alkalinity (or total concentration of carbonate species) and pH are the most influential parameters as they control the amount of dechlorination likely to occur before the minimum design pH is reached. The concentrations of non-chlorinated electron acceptors (i.e., sulfate) are also important because they (i) compete for H_2 and

thus alter the amount of fermentation by-products generated per mol of dechlorination, and (ii) generate alkalinity upon reduction (Robinson et al., in press). Electron potential (pe), the negative logarithm of electron activity, can also be specified for the initial water chemistry. This parameter can be easily calculated from redox potential (Eh) measurements. The model results however are not sensitive to the initial pe value used because as soon as excess H_2 is added to the solution from the overall dechlorination and fermentation reaction (e.g. (3)), reducing conditions are induced and the pe drops accordingly. The partial pressure of dissolved N_2 gas in the influent groundwater can also be specified. This influences the extent of dechlorination likely to occur prior to gas bubble formation and thus the release of $CO_2(g)$. It should be noted that the initial CO_2 partial pressure is already set by specification of the pH and alkalinity (or total concentration of carbonate species).

3.1.2. Minerals

Robinson et al. (in press) showed that calcite and iron oxides are the key crystalline minerals influencing the soil's buffering capacity in a chlorinated solvent treatment zone. Dissolution kinetics for other common crystalline minerals such as silicates are too slow to influence the natural buffering capacity over the typical design residence time for groundwater in the treatment zone (<1 year). As such calcite and iron oxides are the only minerals considered in BUCHLORAC. Simulations performed by Robinson et al. (in press) demonstrated that calcite dissolution is of the order of hours and thus the model assumes that calcite is in equilibrium with the solution. On the other hand, the time scale of iron oxide dissolution is comparable to a typical treatment design time scale. The user must specify the amount of iron oxide present as ferrihydrite, $Fe(OH)_3$, and the amount present as goethite, $FeOOH$. The dissolution rate of ferrihydrite (freshly precipitated) is two orders of magnitude greater than that for well-crystallized stable goethite (Appelo and Postma, 2005). As the dissolution kinetics of these

Fig. 2. Specification of initial water chemistry in BUCHLORAC for Arnold Air Force Base buffer design example (screen shot).

minerals are surface area controlled, the rates increase with the mineral surface area per unit volume of aquifer, and therefore as the moles of mineral initially present increases. Rate expressions and constants adopted are based on Appelo and Postma (2005). The dissolution and subsequent reduction of iron oxides alters the buffer requirement because this process adds alkalinity while consuming H_2 (Robinson et al., submitted for publication). Finally, BUCHLORAC provides for iron sulfide precipitation when the solution becomes oversaturated following iron and sulfate reduction.

3.1.3. Buffer

The user can select either sodium or potassium bicarbonate as the buffering additive. Other buffers such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and lime (CaO) are not included in BUCHLORAC as they are not considered to be practical alternatives. The first two tend to provide unstable pH control while the latter is likely to lead to significant in situ calcite precipitation and subsequent aquifer clogging (McCarty et al., 2007).

Within PHREEQC, we have implemented a modeling approach wherein the amount of buffer needed is calculated using an artificial mineral phase that is composed of the specified buffer. This phase dissolves/precipitates to control the pH when dechlorination reduces the pH below the minimum design value. Normally, the initial groundwater pH is above the minimum design pH, so dechlorination proceeds for a period until the design pH is reached. However, perhaps unintuitively, in the model a small amount of buffer sometimes needs to be added to the initial solution before dechlorination commences. This initial buffer addition is required because of the common ion effect. If the total initial aqueous carbonate concentration is too low, calcite dissolves and the artificial buffer phase simultaneously precipitates to maintain the

design pH. In that case buffer is removed from, rather than added to, the solution. By adding a small amount of buffer to the initial solution, the total aqueous carbonate concentration is increased and calcite dissolution does not occur. Subsequently, dechlorination proceeds and, when the minimum design pH is reached, the artificial buffer phase dissolves (i.e., buffer is added to the solution) to control the pH. The default value for the amount of buffer added before dechlorination commences is 0.02 moles. This value however may be varied depending on the initial solution alkalinity, pH and presence of calcite.

3.1.4. Fermentable organic substrate

As different organic substrates add different amounts of organic acids, carbonate species, and in some cases sodium per mol of H_2 produced from fermentation, the choice of substrate significantly influences the buffer requirements. BUCHLORAC allows the user to select from a list of common substrates including linoleic acid, lactic acid, sodium lactate, butyric acid, methanol, glucose, ethanol and formate. Fermentation reactions used for these substrates are based on standard biochemical pathways (Robinson et al., in press, Table 1).

3.1.5. Operational and design parameters

Additional parameters relevant to a user's specific design and operating conditions that influence the buffer requirements, and thus are considered in BUCHLORAC, are detailed below:

- Minimum design pH. The pH below which dechlorinating microorganisms are inhibited influences not only the extent of dechlorination that will occur before buffer addition is needed, but also the amount of buffer required per mol of dechlorination once this pH is reached. Because the dissociation of weak acids varies with pH, the buffer requirement decreases

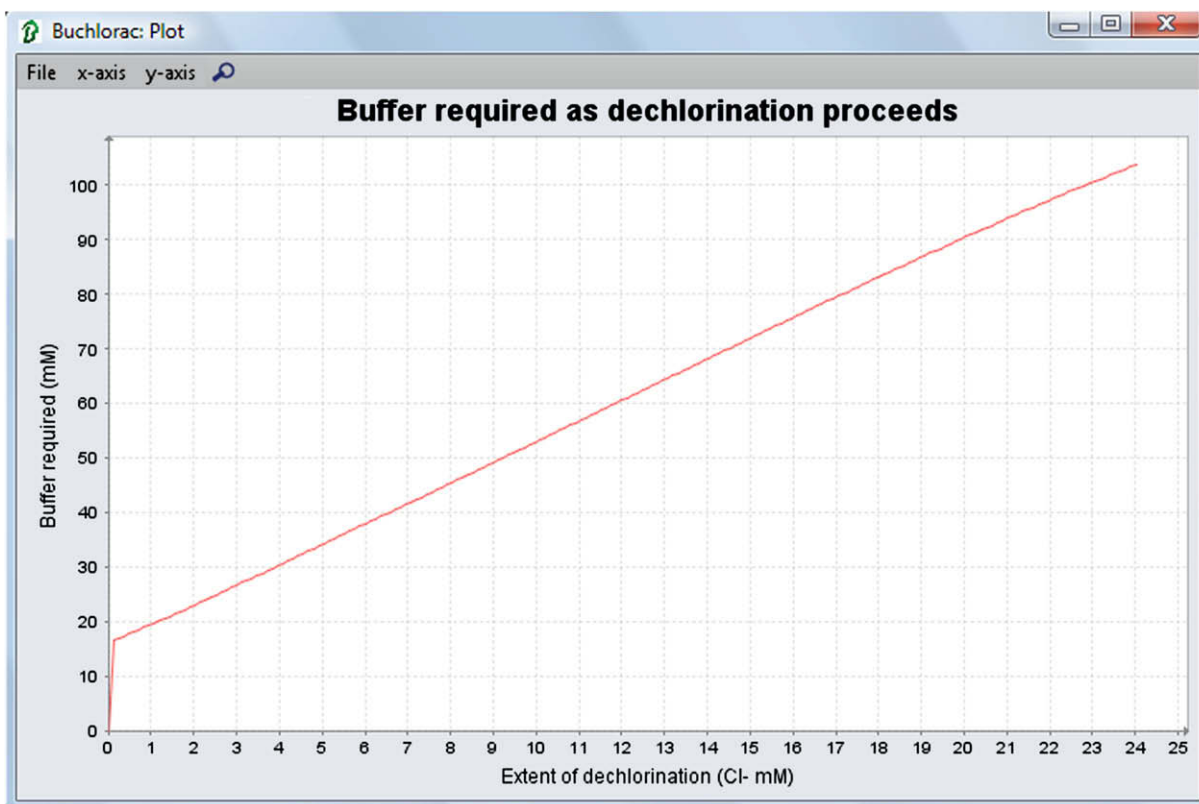


Fig. 3. Buffer requirement as a function of the extent of dechlorination (Cl^- produced) for Arnold Air Force Base buffer design example (screen shot).

significantly if microorganisms are able to tolerate more acidic conditions and the minimum design pH can be lowered (Robinson et al., in press).

- Groundwater residence time. The transit time for groundwater to flow through the DNAPL treatment zone is important relative to the dissolution time scales for ferrihydrite and goethite. Because BUCHLORAC neglects the influence of minerals with slow dissolution rates (e.g., silicate minerals), this value should not be greater than approximately one year. If the model is used for longer periods, the buffer requirement will likely be an over-estimate as silicate minerals may provide additional buffering capacity (Appelo and Postma, 2005).
- Average pressure. For an unconfined aquifer this should be based on the average depth of the DNAPL treatment zone below the water table, and for a confined aquifer on pressure head measurements in the treatment zone. The model allows a gas phase to form when the sum of the partial pressures of dissolved gases formed exceeds this pressure. Gas phase formation, in particular the release of $\text{CO}_2(\text{g})$, lowers the buffer requirement per mol of dechlorination.
- Minimum H_2 efficiency (f_{min}). This is the minimum fraction of H_2 used for dechlorination when non-chlorinated electron acceptors are available. Design factors for f commonly used are of the order of 0.2–0.5 (Parsons Corporation, 2004). The influence of f_{min} on the buffer requirement is complex as it depends on the specific non-chlorinated electron acceptor reduced as each produces different amounts of alkalinity per mol of H_2 consumed.
- Acetate oxidation parameter (p). This parameter specifies the proportion of acetate generated from organic substrate fermentation that is used as a direct electron donor for dechlorination and for the reduction of non-chlorinated electron acceptors. The oxidization of acetate not only reduces the organic substrate requirements, but also reduces the amount of buffer required per mol of dechlorination (Robinson et al., in press).

3.1.6. Extent of dechlorination

Buffer requirements are calculated for a specified amount of dechlorination. This may be entered as either (i) moles of PCE, TCE, DCE and VC that will degrade completely to ethene or, more generally, (ii) total moles of R–Cl that will degrade. When the first option is used, BUCHLORAC calculates the moles of R–Cl to be degraded as $4 \times \text{PCE} + 3 \times \text{TCE} + 2 \times \text{DCE} + 1 \times \text{VC}$.

3.2. Output data

Plots showing the amount of (i) buffer and (ii) organic substrate required as functions of the extent of dechlorination are automatically generated in BUCHLORAC when the PHREEQC model finishes running (e.g., Fig. 3) The user can then select other parameters to plot depending on the specific results they would like to visualize. Output ASCII files generated by a BUCHLORAC run include:

- influent_solution.txt – allows user to check the initial influent solution speciation performed by PHREEQC.
- output_data.txt – selected data is printed to this file at the end of each reaction step, for example the total amount of Cl^- produced from dechlorination, buffer required, pH, amounts of minerals dissolved/precipitated, and concentrations of major aqueous and gaseous species. These data can be accessed for more detailed (graphical) analysis than provided within BUCHLORAC.

- output_detailed.txt – contains detailed model output including all the kinetic, mineral, gas phase and aqueous speciation data for each reaction step.

4. Example field design calculation

To illustrate the use of BUCHLORAC as a design tool we apply the software to conditions relevant to enhanced reductive dechlorination field trials previously conducted at a contaminated chlorinated solvent site at Arnold Air Force Base (Lee et al., 2005). Limited dechlorination was observed during these trials and this may have been due to bacterial inhibition associated with low groundwater pH. Baseline monitoring indicated that the source zone pH was initially as low as 5.0 and that the groundwater acidity was shown to increase further following the injection of a soybean oil emulsion (organic substrate). Sodium bicarbonate (1 g/L) was injected in an emulsion with the soybean oil in one of the field trials, however acidic conditions persisted indicating that this dosage, added only to the soybean oil emulsion, was insufficient for pH control. Here we use BUCHLORAC to estimate the amount of buffer required to increase and subsequently maintain the pH in the remediation zone at 6.5 as dechlorination proceeds. Site information was sourced from Lee et al. (2003, 2005) and the parameters used in BUCHLORAC are provided in Table 2. The results indicate that for these operating conditions 8.7 g/L (104 mmol/L) sodium

Table 2
Input parameters for Arnold Air Force Base buffer design example.

Parameter	Value	Comment/Reference
<i>Initial water chemistry</i>		
pH	5.5	Lee et al. (2003, 2005)
Sulfate	157 mg/L	Lee et al. (2003, 2005)
K^+	65.5 mM	Concentration adjusted to charge balance solution
Dissolved N_2 gas	0.79 (atm)	Assumes dissolved N_2 is conservative (Amos and Mayer, 2006) and that groundwater N_2 is equilibrated with the atmosphere N_2
Alkalinity	100 mg/L	Value assumed but variation in alkalinity from this value can simply be subtracted from the total bicarbonate requirement estimated
<i>Minerals</i>		
Calcite	Negligible	Site mineralogy data not provided. Sensitivity analysis performed
Goethite	Negligible	Site mineralogy data not provided. Measured Fe^{2+} concentrations <0.3 mM (Lee et al., 2005)
Ferrihydrite	Negligible	Site mineralogy data not provided. Measured Fe^{2+} concentrations <0.3 mM (Lee et al., 2005)
Buffer	NaHCO_3	Lee et al. (2003, 2005)
Organic substrate	Linoleic acid	Main constituent of soybean oil (Lee et al., 2005)
<i>Operational parameters</i>		
Minimum design pH	6.5	McCarty et al. (2007)
Residence time (d)	100	Value assumed but as goethite and ferrihydrite are not present (dissolution rate-controlled), this time is irrelevant
Average pressure (atm)	1.2	Lee et al. (2003), 2 m below water table
f_{min}	0.2	Typical value from previous study (Parsons Corporation, 2004; Robinson et al., in press)
p	0.5	Typical value from previous study (Robinson et al., in press)
Extent of dechlorination	24 mM	Complete degradation of TCE at its solubility limit. This is assumed to be the maximum dechlorination extent if the remediation scheme is successful

bicarbonate should be added to the groundwater flowing through the treatment zone. This dosage rate assumes that the remediation scheme is successful with 24 mmol of R-Cl degraded per L of water flowing through the DNAPL zone. The model indicates that 1.4 g/L sodium bicarbonate is required just to increase the influent pH (5.5) to a suitable level for dechlorinating bacteria (6.5). Although this design prediction assumes that there is negligible naturally occurring calcite, BUCHLORAC predicts that, even with an excess of calcite present, the buffer requirement only reduces to 8.2 g/L. This is because calcite's buffering capacity is limited by solubility constraints. The results also show significant sulfate reduction and that a gas phase may form rapidly upon buffer addition. Due to the low measured groundwater iron(II) concentrations (Lee et al., 2003, 2005), it is assumed that iron oxide reduction at the site is negligible.

5. Concluding remarks

With recent studies indicating that the implementation of pH control strategies may be crucial to the design of successful enhanced reductive source zone dechlorination treatment schemes, BUCHLORAC is likely to be a useful design tool. The software was developed based on detailed conceptual understanding of the main processes influencing the acidity and thus buffer requirements in dechlorinating treatment zones. Application of BUCHLORAC to estimate the amount of buffer required to ensure sustained dechlorination at a contaminated chlorinated solvent site illustrates that it is a practical and easy-to-use software tool that can provide detailed design estimates for field dechlorination projects. Although the example application is for illustrative purposes, it reveals an order of magnitude difference in the model-predicted buffer needs and that reported in a field application.

Acknowledgements

The impetus for BUCHLORAC was provided by the SABRE (Source Area BioREmediation, http://www.claire.co.uk/index.php?option=com_content&task=view&id=53&Itemid=47) project. The authors acknowledge the valuable advice provided by members of this project, in particular Perry McCarty, Mike Lee, Mark Harkness and David Ellis. Java programming was carried out by Olivier Gobet. Support from BBSRC BB/B519076/1 and SNF 200021_120160 is acknowledged.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.envsoft.2009.03.012](https://doi.org/10.1016/j.envsoft.2009.03.012).

References

- Adamson, D.A., Lyon, D.Y., Hughes, J.B., 2004. Flux and product distribution during biological treatment of tetrachloroethene dense non-aqueous-phase liquid. *Environmental Science and Technology* 38 (7), 2021–2028.
- Adamson, D.T., McDade, J.M., Hughes, J.B., 2003. Inoculation of DNAPL source zone to initiate reductive dechlorination of PCE. *Environmental Science and Technology* 37 (11).
- Allison, J.D., Brown, D.S., Novo-Gradac, K.J., 1990. MINTEQA2/PRODEFA2 – A Geochemical Assessment Model for Environmental Systems – Version 3.0 User's Manual. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia.
- Amos, R.T., Mayer, K.U., 2006. Investigating the role of gas bubble formation and entrapment in contaminated aquifers: reactive transport modelling. *Journal of Contaminant Hydrology* 87, 123–154.
- Appelo, C.A.J., Postma, D., 2005. *Geochemistry, Groundwater and Pollution*, second ed. A.A. Balkema Publishers, Amsterdam, Netherlands.
- Aulenta, F., Majone, M., Tandoi, V., 2006. Enhanced anaerobic bioremediation of chlorinated solvents: environmental factors influencing microbial activity and their relevance under field conditions. *Journal of Chemical Technology and Biotechnology* 81, 1463–1474, doi:10.1002/jctb.1567.
- Carr, C.S., Hughes, J.B., 1998. Enrichment of high-rate PCE dechlorination and comparative study of lactate, methanol, and hydrogen as electron donors to sustain activity. *Environmental Science and Technology* 32 (12), 1817–1824.
- Ellis, D.E., Lutz, E.J., Odom, J.M., Buchanan, R.J., Bartlett, C.L., Lee, M.D., Harkness, M.R., Dewerd, K.A., 2000. Bioaugmentation for accelerated in situ anaerobic bioremediation. *Environmental Science and Technology* 34 (11), 2254–2260.
- Lee, M.D., Beckwith, W., Borden, R.C., Lieberman, M.T., Haas, P., Becvar, E.D.K., Dobson, K., Sandlin, G.J., 2005. Vegetable oil pilots to enhance DNAPL sequestration and reductive dechlorination. In: *Proceedings of the Eighth International In Situ and On-site Bioremediation Symposium*. Battelle Press, Baltimore, Maryland, USA.
- Lee M.D., Lieberman M.T., Borden R.C., 2003. Final summary of proposed works for technology application of low cost emplacement of slowly-soluble organic substrate for enhanced in situ reductive dechlorination of halogenated aliphatic hydrocarbons Arnold Air Force Base, Tennessee. Prepared for Air Force Center for Environmental Excellence and Arnold Engineering Development Center, Brooks City-Base, Texas, USA.
- Major, D.W., McMaster, M.L., Cox, E.E., Edwards, E.A., Dworatzek, S.M., Hendrickson, E.R., Starr, M.G., Payne, J.A., Buonamici, L.W., 2002. Field demonstration of successful bioaugmentation to achieve dechlorination of tetrachloroethene to ethene. *Environmental Science and Technology* 36 (23), 5106–5116.
- McCarty, P.L., 1997. Breathing with chlorinated solvents. *Science* 276 (5318), 1521–1522.
- McCarty, P.L., Chu, M.Y., Kitandis, P.K., 2007. Electron donor and pH relationships for biologically enhanced dissolution of chlorinated solvent DNAPL in groundwater. *European Journal of Soil Biology* 43 (5–6), 276–282.
- National Research Council, 2004. *Contaminants in the subsurface: source zone assessment and remediation*. Washington, DC.
- Parkhurst, D.L., Appelo, C.A.J., 1999. *User's Guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations*. Water-Resources Investigations Report 99-4259. US Geological Survey, Denver, Colorado.
- Parsons Corporation, 2004. *Principles and practices of enhanced anaerobic bioremediation of chlorinated solvents*. Prepared for: Air Force Center for Environmental Excellence, Brooks City-Base, Texas, Naval Facilities Engineering Service Center, Port Hueneme, California and Environmental Security Technology Certification Program, The National Academies Press, Arlington, Virginia, USA.
- Rivett, M., Shepherd, K., Keays, L., Brennan, A., 2005. Chlorinated solvents in the Birmingham aquifer, UK: 1986–2001. *Quarterly Journal of Engineering Geology and Hydrogeology* 38, 337–350.
- Robinson C., Barry D.A., McCarty P.L., Gerhard J.I., Kouznetsova I. pH control for enhanced reductive source zone bioremediation of chlorinated solvents. *Science of the Total Environment*, in press, doi:10.1016/j.scitotenv.2009.03.029.
- Yang, Y., McCarty, P.L., 2002. Comparison between donor substrates for biologically enhanced tetrachloroethene DNAPL dissolution. *Environmental Science and Technology* 36, 3400–3404.