

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

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10 **Software Availability**

11 Software title: BUCHLORAC

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16 Software required: Java Runtime Environment 6.0, Windows 2000/XP/Vista

17 Availability: Supplementary material (free to use)

18

19 **Abstract**

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

35 *Keywords:* alkalinity, bicarbonate, dechlorination, dehalogenation, PHREEQC, BUCH-
36 LORAC, TCE, PCE, contaminated aquifer, remediation, DNAPL

37

38 **1. Introduction**

39 Chlorinated solvents, such as tetrachloroethene (PCE) and trichloroethene (TCE), are
40 widespread contaminants due to their extensive use, accidental release, and improper
41 disposal over the last century (National Research Council, 2004). They are amongst the
42 most hazardous groundwater contaminants, and in addition, because they are often
43 present in the subsurface as dense nonaqueous phase liquids (DNAPLs), they are also
44 amongst the most persistent (National Research Council, 2004; Rivett et al., 2005).
45 Reductive bioremediation is now recognized as a promising cost-effective technology for
46 the in-situ clean-up of chlorinated solvent source areas (McCarty, 1997; Ellis et al., 2000;
47 Major et al., 2002; Yang and McCarty, 2002; Adamson et al., 2003). In recent years in-
48 creased understanding of dechlorinating microorganisms and the selection of suitable
49 fermentable organic substrates has led to more rapid dechlorination rates and considera-
50 bly improved the extent of degradation of PCE and TCE to lesser chlorinated compounds.
51 Nevertheless, in spite of these advancements, complete remediation is still often hindered
52 at many sites due to the development of unfavorable aquifer conditions, in particular low
53 groundwater pH, which inhibits the activity of the dechlorinating microorganisms (Carr
54 and Hughes, 1998; Aulenta et al., 2006).

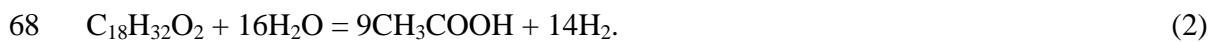
55 **TABLE 1 NEAR HERE**

56 The major processes influencing the amount of acidity generated in the DNAPL
57 treatment zone during enhanced reductive dechlorination have been investigated by Ro-
58 binson et al. (2009). A summary of these processes is provided in Table 1. Reductive
59 dechlorination is a step-wise process with PCE converted to TCE to dichloroethene

60 (DCE) to vinyl chloride (VC), and finally to ethene. Each step involves the addition of
61 electron donor (hydrogen, H₂) and production of hydrochloric acid (HCl). The reduction
62 of R-Cl, a generic chlorinated ethene compound, is given by:



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



69 Dechlorinating microorganisms must compete for the H₂ produced from fermenta-
70 tion with microorganisms associated with the reduction of non-chlorinated electron ac-
71 ceptors (e.g., sulfate, iron(III)). These competing non-chlorinated reduction reactions not
72 only increase the organic substrate demand but also significantly influence the amount of
73 acidity produced (McCarty et al., 2007; Robinson et al., 2009). To ensure effective dech-
74 lorination it is necessary to consider the soil's buffering capacity to determine whether
75 there is adequate natural alkalinity available to control the acidity generated. Where the
76 natural buffering is likely to be exceeded, a pH control system may be necessary. This
77 typically involves the addition of a buffer such as potassium or sodium bicarbonate
78 (KHCO₃, NaHCO₃). Groundwater pH is strongly controlled by the dissolved carbonate
79 equilibria and the addition of bicarbonate offsets the impact of the higher dissolved CO₂
80 concentrations and therefore neutralizes the pH. With recent studies demonstrating that
81 significant acidification of the source zone may occur even in relatively well buffered

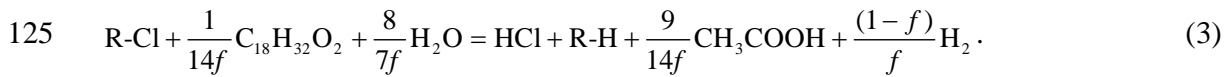
82 soils (Adamson et al., 2004; McCarty et al., 2007; Robinson et al., 2009), buffer dosage
83 systems may be a crucial element in the design of a successful remediation strategy.

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

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

97 To demonstrate application of BUCHLORAC an example is presented where the soft-
98 ware is used to estimate the buffer requirement for a contaminated chlorinated solvent
99 site where limited dechlorination rates have previously been observed mainly due to acid-
100 ic groundwater conditions.

101 2. Description of BUCHLORAC



126 Overall reactions for different organic substrates considered in BUCHLORAC are pro-
127 vided in its Help documentation as well as Robinson et al. (2009). The modeling ap-
128 proach is to assume a given amount of R-Cl degrades and to follow this overall reaction
129 in steps. The solution is speciated at the end of each reaction step and in doing so the sur-
130 plus H₂ produced in (3) is consumed by the available non-chlorinated electron acceptors.
131 Other reactions affecting the solution chemistry also occur: minerals are allowed to dis-
132 solve and/or precipitate and gas is released if the sum of the partial pressures of all dis-
133 solved gases present exceeds a specified total pressure. To perform these calculations
134 PHREEQC uses a geochemical database that contains thermodynamic data for aqueous
135 species, and gas and mineral phases. The database is that used with MINTEQ (Allison et
136 al., 1990) with the inclusion of mineral dissolution/precipitation kinetics. When the avail-
137 ability of non-chlorinated electron acceptors is limited, *f* is automatically adjusted such
138 that only the H₂ required to reduce the available competing electron acceptors is pro-
139 duced in (3). The main task of the program occurs when the pH drops to the user-
140 specified minimum value, following which the program calculates the amount of buffer
141 needed to maintain this pH.

142 **3. BUCHLORAC Features**

143 **3.1 Input parameters**

144 The user options available in BUCHLORAC are based on extensive use of the
145 geochemical model and thus our understanding of the main factors influencing the buffer

146 requirements (Table 1, Robinson et al., 2009). Default parameter values are provided in
147 BUCHLORAC that can be used when values pertaining to the user's specific operating
148 conditions are unknown.

149 3.1.1 Initial Water Chemistry

150 The user is able to specify their influent (background) groundwater chemistry, in-
151 cluding concentrations of major cations and anions, alkalinity, pH and temperature (e.g.,
152 Figure 2). Here the alkalinity (or total concentration of carbonate species) and pH are the
153 most influential parameters as they control the amount of dechlorination likely to occur
154 before the minimum design pH is reached. The concentrations of non-chlorinated elec-
155 tron acceptors (i.e., sulfate) are also important because they (i) compete for H_2 and thus
156 alter the amount of fermentation by-products generated per mol of dechlorination, and (ii)
157 generate alkalinity while being reduced (Robinson et al., 2009). Electron potential (pe),
158 the negative logarithm of electron activity, can also be specified for the initial water che-
159 mistry. This parameter can be easily calculated from redox potential (Eh) measurements.
160 The model results however are not sensitive to the initial pe value used because as soon as
161 excess H_2 is added to the solution from the overall dechlorination and fermentation reac-
162 tion (e.g. (3)), reducing conditions are induced and the pe drops accordingly. The partial
163 pressure of dissolved N_2 gas in the influent groundwater can also be specified. This influ-
164 ences the extent of dechlorination likely to occur prior to gas bubble formation and thus
165 the release of $CO_2(g)$. It should be noted that the initial CO_2 partial pressure is already set
166 by specification of the pH and alkalinity (or total concentration of carbonate species).

167

FIGURE 2 NEAR HERE

168 3.1.2 *Minerals*

169 Robinson et al. (2009) showed that calcite and iron oxides are the key crystalline
170 minerals influencing the soil's buffering capacity in a chlorinated solvent treatment zone.
171 Dissolution kinetics for other common crystalline minerals such as silicates are too slow
172 to influence the natural buffering capacity over the typical design residence time for
173 groundwater in the treatment zone (< 1 year). As such calcite and iron oxides are the only
174 minerals considered in BUCHLORAC. Simulations performed by Robinson et al. (2009)
175 demonstrated that calcite dissolution is of the order of hours and thus the model assumes
176 that calcite is in equilibrium with the solution. On the other hand, the time scale of iron
177 oxide dissolution is comparable to a typical treatment design time scale. The user must
178 specify the amount of iron oxide present as ferrihydrite, $\text{Fe}(\text{OH})_3$, and the amount present
179 as goethite, FeOOH . The dissolution rate of ferrihydrite (freshly-precipitated) is two or-
180 ders of magnitude greater than that for well-crystallized stable goethite (Appelo and
181 Postma, 2005). As the dissolution kinetics of these minerals are surface area controlled,
182 the rates increase with the mineral surface area per unit volume of aquifer, and therefore
183 as the moles of mineral initially present increases. Rate expressions and constants
184 adopted are based on Appelo and Postma (2005). The dissolution and subsequent reduc-
185 tion of iron oxides alters the buffer requirement because this process adds alkalinity while
186 consuming H_2 (Robinson et al., 2009). Finally, BUCHLORAC provides for iron sulfide
187 precipitation when the solution becomes oversaturated following iron and sulfate reduc-
188 tion.

189 3.1.3 *Buffer*

190 The user can select either sodium or potassium bicarbonate as the buffering addi-
191 tive. Other buffers such as sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃) and
192 lime (CaO) are not included in BUCHLORAC as they are not considered to be practical
193 alternatives. The first two tend to provide unstable pH control while the latter is likely to
194 lead to significant in situ calcite precipitation (McCarty et al., 2007).

195 Within PHREEQC, we have implemented a modeling approach wherein the
196 amount of buffer needed is calculated using an artificial mineral phase that is composed
197 of the specified buffer. This phase dissolves/precipitates to control the pH when dechlori-
198 nation reduces the pH below the minimum design value. Normally, the initial groundwa-
199 ter pH is above the minimum design pH, so dechlorination proceeds for a period until the
200 design pH is reached. However, perhaps unintuitively, in the model a small amount of
201 buffer sometimes needs to be added to the initial solution before dechlorination com-
202 mences. This initial buffer addition is required because of the common ion effect. If the
203 total initial aqueous carbonate concentration is too low, calcite dissolves and the artificial
204 buffer phase simultaneously precipitates to maintain the design pH. In that case buffer is
205 removed from, rather than added to, the solution. By adding a small amount of buffer to
206 the initial solution, the total aqueous carbonate concentration is increased and calcite dis-
207 solution does not occur. Subsequently, dechlorination proceeds and, when the minimum
208 design pH is reached, the artificial buffer phase dissolves (i.e., buffer is added to the solu-
209 tion) to control the pH. The default value for the amount of buffer added before dechlori-
210 nation commences is 0.02 moles. This value however may be varied depending on the
211 initial solution alkalinity, pH and presence of calcite.

212 3.1.4 *Fermentable organic substrate*

213 As different organic substrates add different amounts of organic acids, carbonate
214 species, and in some cases sodium per mol of H₂ produced from fermentation, the choice
215 of substrate significantly influences the buffer requirements. BUCHLORAC allows the
216 user to select from a list of common substrates including linoleic acid, lactic acid, sodium
217 lactate, butyric acid, methanol, glucose, ethanol and formate. Fermentation reactions used
218 for these substrates are based on standard biochemical pathways (Robinson et al., 2009,
219 Table 1).

220 3.1.5 Operational and design parameters

221 Additional parameters relevant to a user's specific design and operating condi-
222 tions that influence the buffer requirements, and thus are considered in BUCHLORAC,
223 are detailed below:

- 224 • Minimum design pH. The pH below which dechlorinating microorganisms are
225 inhibited influences not only the extent of dechlorination that will occur before
226 buffer addition is needed, but also the amount of buffer required per mol of dech-
227 lorination once this pH is reached. Because the dissociation of weak acids varies
228 with pH, the buffer requirement decreases significantly if microorganisms are
229 able to tolerate more acidic conditions and the minimum design pH can be lo-
230 wered (Robinson et al., 2009).

- 231 • Groundwater residence time. The transit time for groundwater to flow through the
232 DNAPL treatment zone is important relative to the dissolution time scales for fer-
233 rrihydrite and goethite. Because BUCHLORAC neglects the influence of minerals
234 with slow dissolution rates (e.g., silicate minerals), this value should not be great-

235 er than approximately one year. If the model is used for longer periods, the buffer
236 requirement will likely be an over-estimate, as silicate minerals may provide addi-
237 tional buffering capacity (Appelo and Postma, 2005).

238 • Average pressure. For an unconfined aquifer this should be based on the average
239 depth of the DNAPL treatment zone below the water table, and for a confined
240 aquifer on pressure head measurements in the treatment zone. The model allows a
241 gas phase to form when the sum of the partial pressures of dissolved gases formed
242 exceeds this pressure. Gas phase formation, in particular the release of CO₂(g),
243 lowers the buffer requirement per mol of dechlorination.

244 • Minimum H₂ efficiency (f_{min}). This is the minimum fraction of H₂ used for dech-
245 lorination when non-chlorinated electron acceptors are available. Design factors
246 for f commonly used are of the order of 0.2 to 0.5 (Parsons Corporation, 2004).
247 The influence of f_{min} on the buffer requirement is complex as it depends on the
248 specific non-chlorinated electron acceptor reduced as each produces different
249 amounts of alkalinity per mol of H₂ consumed.

250 • Acetate oxidation parameter (p). This parameter specifies the proportion of ace-
251 tate generated from organic substrate fermentation that is used as a direct electron
252 donor for dechlorination and for the reduction of non-chlorinated electron accep-
253 tors. The oxidization of acetate not only reduces the organic substrate require-
254 ments, but also reduces the amount of buffer required per mol of dechlorination
255 (Robinson et al., 2009).

256 3.1.6 Extent of dechlorination

257 Buffer requirements are calculated for a specified amount of dechlorination. This
258 may be entered as either (i) moles of PCE, TCE, DCE and VC that will degrade com-
259 pletely to ethene or, more generally, (ii) total moles of R-Cl that will degrade. When the
260 first option is used, BUCHLORAC calculates the moles of R-Cl to be degraded as $4 \times$
261 $\text{PCE} + 3 \times \text{TCE} + 2 \times \text{DCE} + 1 \times \text{VC}$.

262 **3.2 Output data**

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

- 268 • influent_solution.txt - permits checking of the initial influent solution speciation
269 performed by PHREEQC.
- 270 • output_data.txt – selected data is printed to this file at the end of each reaction
271 step, for example the total amount of Cl^- produced from dechlorination, buffer re-
272 quired, pH, amounts of minerals dissolved/precipitated, and concentrations of ma-
273 jor aqueous and gaseous species. These data can be accessed for more detailed
274 (graphical) analysis than provided within BUCHLORAC.
- 275 • output_detailed.txt – contains detailed model output including all the kinetic,
276 mineral, gas phase and aqueous speciation data for each reaction step.

277 **FIGURE 3 NEAR HERE**

278 4. Example field design calculation

279 To illustrate the use of BUCHLORAC as a design tool we apply the software to
280 conditions relevant to enhanced reductive dechlorination field trials previously conducted
281 at a contaminated chlorinated solvent site at Arnold Air Force Base (Lee et al., 2005).
282 Limited dechlorination was observed during these trials and this may have been due to
283 bacterial inhibition associated with low groundwater pH. Baseline monitoring indicated
284 that the source zone pH was initially as low as 5.0 and that the groundwater acidity was
285 shown to increase further following the injection of a soybean oil emulsion (organic sub-
286 strate). Sodium bicarbonate (1 g/L) was injected in an emulsion with the soybean oil in
287 one of the field trials, however acidic conditions persisted indicating that this dosage,
288 added only to the soybean oil emulsion, was insufficient for pH control. Here we use
289 BUCHLORAC to estimate the amount of buffer required to increase and subsequently
290 maintain the pH in the remediation zone at 6.5 as dechlorination proceeds. Site informa-
291 tion was sourced from Lee et al. (2003; 2005) and the parameters used in BUCHLORAC
292 are provided in Table 2. The results indicate that for these operating conditions 8.7 g/L
293 (104 mmol/L) sodium bicarbonate should be added to the groundwater flowing through
294 the treatment zone. This dosage rate assumes that the remediation scheme is successful
295 with 24 mmol of R-Cl degraded per L of water flowing through the DNAPL zone. The
296 model indicates that 1.4 g/L sodium bicarbonate is required just to increase the influent
297 pH (5.5) to a suitable level for dechlorinating bacteria (6.5). Although this design predic-
298 tion assumes that there is negligible naturally occurring calcite, BUCHLORAC predicts
299 that, even with an excess of calcite present, the buffer requirement only reduces to 8.2
300 g/L. This is because calcite's buffering capacity is limited by solubility constraints. The

301 results also show significant sulfate reduction and that a gas phase may form rapidly upon
302 buffer addition. Due to the low measured groundwater iron(II) concentrations (Lee et al.,
303 2003; 2005), it is assumed that iron oxide reduction at the site is negligible.

304 **TABLE 2 NEAR HERE**

305 **5. Concluding Remarks**

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

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319 tion, [_http://www.claire.co.uk/index.php?option=com_content&task=view&id=53&Ite-](http://www.claire.co.uk/index.php?option=com_content&task=view&id=53&Itemid=47)
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387

388 **Table 1.** Main factors influencing groundwater acidity during enhanced reductive dechloro-
 389 rination (arrows indicate the direction of pH change).

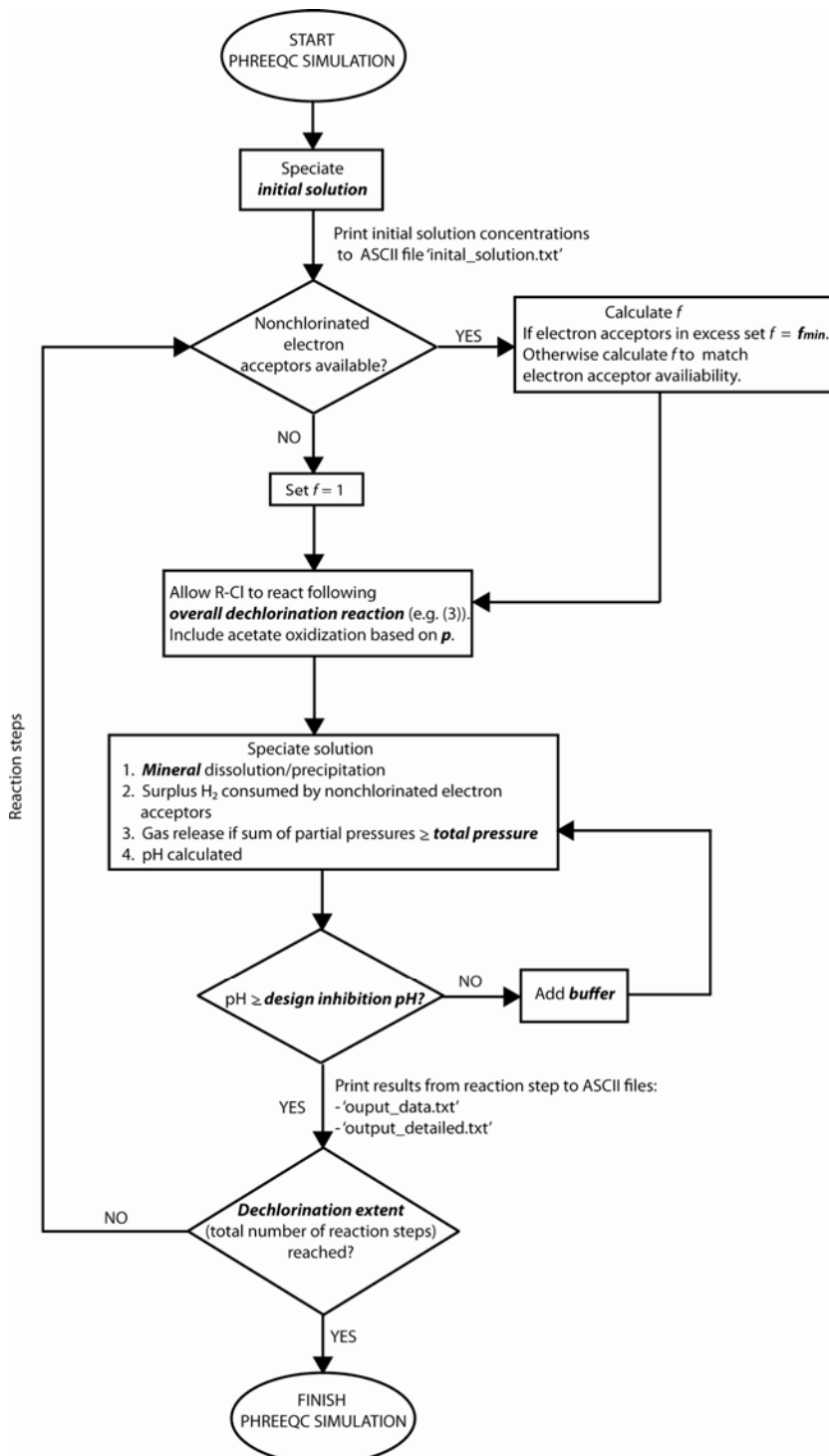
Process	Influence
Dechlorination	pH ↓
Fermentation	Depends on fermentation products of organic substrate used: Acetate species - pH ↓ Carbonate species - pH ↓ Sodium ion - pH ↑
Sulfate reduction	Direct effect is pH ↑ Overall effect including supply of additional H ₂ depends on organic substrate used
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
Release of CO ₂ (g)	pH ↑

390

391 **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)
<i>Buffer</i>	NaHCO ₃	Lee et al. (2003; 2005)
<i>Organic substrate</i>	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., 2009)
p	0.5	Typical value from previous study (Robinson et al., 2009)
<i>Extent of dechlorination</i>	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

392

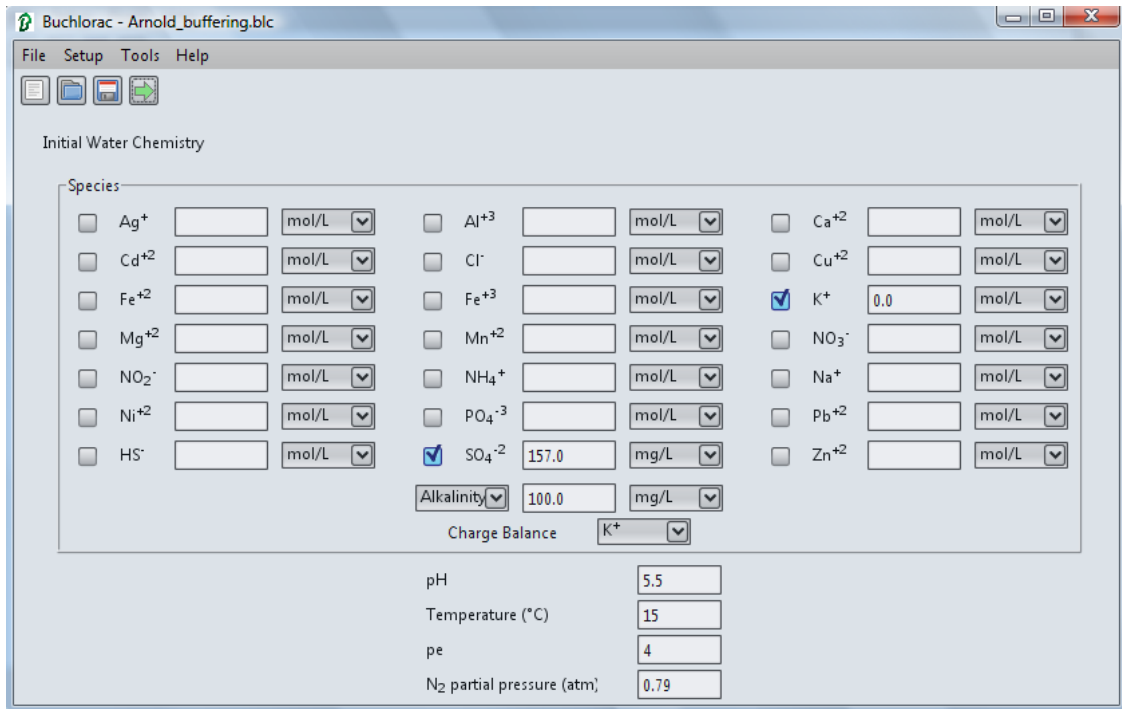


393

394 **Figure 1.** Flow chart of the PHREEQC model algorithm that performs the calculations

395 within BUCHLORAC. Bold italic text indicates parameters that are specified by the user

396 through BUCHLORAC. A description of the algorithm is provided in Section 2.

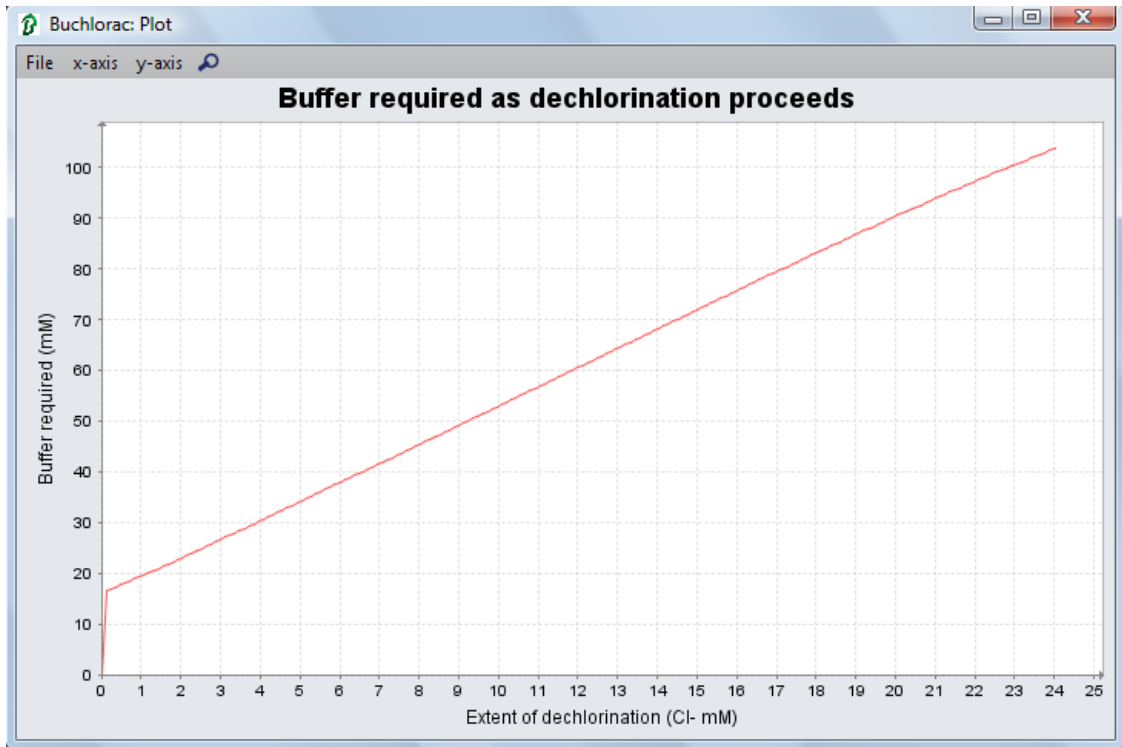


397

398 **Figure 2.** Specification of initial water chemistry in BUCHLORAC for Arnold Air Force

399 Base buffer design example (screen shot).

400



401

402 **Figure 3.** Buffer requirement as a function of the extent of dechlorination (Cl⁻ produced)

403 for Arnold Air Force Base buffer design example (screen shot).