

1 **Transport and degradation of perchlorate in deep vadose zone: implications**  
2 **from direct observations during bioremediation treatment**

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7 monitoring

8 **Abstract**

9 An in situ bioremediation experiment of a deep vadose zone (~40 m) contaminated  
10 with a high concentration of perchlorate ( $>25,000 \text{ mg L}^{-1}$ ) was conducted through a  
11 full-scale field operation. Favorable environmental conditions for microbiological  
12 reduction of perchlorate were sought by infiltrating an electron donor-enriched water  
13 solution using drip irrigation underlying an airtight sealing liner. A vadose-zone  
14 monitoring system (VMS) was used for real-time tracking of the percolation process,  
15 the penetration depth of dissolved organic carbon (DOC), and the variation in  
16 perchlorate concentration across the entire soil depth. The experimental conditions for  
17 each infiltration event were adjusted according to insight gained from data obtained  
18 by the VMS in previous stages. Continuous monitoring of the vadose zone indicated  
19 that in the top 13 m of the cross section, perchlorate concentration is dramatically  
20 reduced from thousands of milligrams per liter to near-detection limits with a  
21 concurrent increase in chloride concentration. Nevertheless, in the deeper parts of the  
22 vadose zone ( $<17 \text{ m}$ ), perchlorate concentration increased, suggesting its mobilization  
23 down through the cross section. Breakthrough of DOC and bromide at different

24 depths across the unsaturated zone showed limited migration capacity of biologically  
25 consumable carbon and energy sources due to their enhanced biodegradation in the  
26 upper soil layers. Nevertheless, the increased DOC concentration with concurrent  
27 reduction in perchlorate and increase in the chloride-to-perchlorate ratio in the top 13  
28 m indicate partial degradation of perchlorate in this zone. There was no evidence of  
29 improved degradation conditions in the deeper parts where the initial concentrations  
30 of perchlorate were significantly higher.

## 31 **1 Introduction**

32 In situ bioremediation of a contaminated unsaturated zone (also termed vadose zone)  
33 depends mainly on the ability to control the hydrological, physical and chemical  
34 conditions in the subsurface (Bombach et al., 2010; EPA, 2015; Höhener and Ponsin,  
35 2014). Chemical and hydrological manipulations are primarily aimed at enhancing the  
36 activity of specific indigenous degrading bacteria. The optimal conditions for specific  
37 contaminants' degradation are usually determined in microcosm experiments, where  
38 the preferred electron donor and acceptor for degradation can be controlled and  
39 examined (Gal et al., 2008; Megharaj et al., 2011; Sagi-Ben Moshe et al., 2012). The  
40 optimal degradation conditions, evaluated through laboratory experiments, usually  
41 form the basis for selecting a strategy for in situ remediation in field-scale operations.  
42 Nevertheless, implementation of desired biodegradation conditions in the deep vadose  
43 zone through full-scale field setups requires control of the vadose zone  
44 hydrogeochemical conditions. This is often achieved through either infiltration of  
45 water enriched with electron donors or nutrients (Battey et al., 2007; EPA, 2004;  
46 Frankel and Owsianiak, 2005), or injection of a gaseous mixture capable of promoting  
47 optimal biogeochemical conditions for microbial pollutant degradation (Evans et al.,

48 2011; Evans and Trute, 2006). Due to the complex nature of flow and transport  
49 processes in the unsaturated zone, application of water with specific chemical  
50 conditions near land surface does not necessarily result in promoting the desired  
51 geochemical and hydraulic conditions in deeper parts of the vadose zone (Allaire et  
52 al., 2009; Flury and Wai, 2003; Jarvis, 2007; Rimon et al., 2011a). Therefore, in the  
53 vadose zone, and particularly in its deeper parts, a proper understanding of the  
54 transport process is key to the success of in situ remediation operations (Baram et al.,  
55 2012a; Dahan et al., 2009; Kurtzman et al., 2016; Rimon et al., 2011a).

56 Assessment of water percolation and solute transport in the vadose zone is considered  
57 a major challenge in hydrological sciences. It is often characterized by unstable flow  
58 that is highly sensitive to hydraulic, chemical and microbial conditions (Bautersa et  
59 al., 2000; Dahan et al., 2009; DiCarlo, 2007; Germann and al Hagrey, 2008; Hallett et  
60 al., 2013; Rimon et al., 2011a; Sher et al., 2012; Stumpp et al., 2009). Moreover, the  
61 chemical composition of the percolating water [e.g., dissolved organic carbon (DOC),  
62 oxygen and nutrients] is subjected to frequent changes due to natural hydroclimatic  
63 and biological cycles (Stumpp et al., 2009, 2012). Accordingly, contaminant  
64 attenuation in the vadose zone is dependent on the complex hydrological, chemical  
65 and biological states of the sediment. Continuous measurements of the hydrological  
66 and chemical properties of the unsaturated zone may be achieved with a vadose-zone  
67 monitoring system (VMS) (Dahan et al., 2009). The VMS provides high-resolution  
68 measurements of variation in sediment water content (Dahan et al., 2008; Rimon et  
69 al., 2007) and evolution of the pore water's chemical composition across the  
70 unsaturated profile (Rimon et al., 2011a; Dahan et al., 2014; Turkeltaub et al., 2014,  
71 2016).

72 Perchlorate is an environmental pollutant that is often associated with the explosives  
73 manufacturing industry (Roote, 2001; Urbansky, 2002; Trumpolt et al., 2005). It is  
74 mostly produced, and consequently released to the environment as ammonium  
75 perchlorate. Its high solubility ( $220 \text{ g L}^{-1}$ ) and stability in aerobic environments makes  
76 it very mobile and persistent in the subsurface (Motzer, 2001; Urbansky and Brown,  
77 2003). Microbial reduction of perchlorate to harmless chloride and oxygen in the  
78 unsaturated zone requires elevated water content, negative redox potential, available  
79 electron donors and the presence of suitable indigenous bacteria (Coates and  
80 Achenbach, 2004). In the vadose zone, natural attenuation and biodegradation of  
81 perchlorate are considered very limited (Gal et al., 2009). Nevertheless, studies have  
82 shown that perchlorate can be metabolized in unsaturated soil whenever reducing  
83 conditions ( $<110 \text{ mV}$ ) (Attaway and Smith, 1993; Shrouf and Parkin, 2006) are  
84 achieved and an available electron donor is introduced (Tipton et al., 2003; Frankel  
85 and Owsianiak, 2005; Nozawa-Inoue et al., 2005; Evans and Trute, 2006; Cai et al.,  
86 2010).

87 Here, the efficiency of a remediation operation of a perchlorate-contaminated vadose  
88 zone was assessed using a VMS, which provided continuous information on the  
89 chemical composition of the vadose-zone pore water. Promotion of perchlorate-  
90 degrading conditions in the vadose zone was based on infiltration of water enriched  
91 with ethanol (as a source of electron donor) from land surface. Real-time information  
92 on the depth of the enriched water's propagation, along with variations in the  
93 concentrations of perchlorate, chloride and bromide (applied as a tracer), was used to  
94 assess transport and degradation of perchlorate across the unsaturated profile. Water-  
95 and ethanol-application strategies were adjusted in each flow phase to obtain real-time  
96 feedback on the chemical and hydrological state of the vadose zone.

## 97 **2 Study site**

98 The study area is located in the central part of the Israeli coastal plain, east of the city  
99 of Ramat Hasharon. The site is a former unlined earthen pond that was used to store  
100 industrial wastewater for several decades. A hydrogeological survey conducted in the  
101 study area revealed substantial perchlorate contamination in the vadose zone and  
102 groundwater under the pond area (Gal et al., 2008, 2009). It was concluded that  
103 percolation of untreated wastewater from the ponds had crossed the 40m thick vadose  
104 zone and created a large perchlorate pollution plume in the underlying phreatic aquifer  
105 with concentrations exceeding  $1,000 \text{ mg L}^{-1}$ . In the vadose zone, however, the  
106 investigation revealed extreme perchlorate pollution, reaching concentrations  
107 exceeding  $2,000 \text{ mg kg}^{-1}$  dry soil (equivalent to  $\sim 25,000 \text{ mg L}^{-1}$  in the sediment pore  
108 water), along with high total salinity and chloride concentration exceeding  $25,000 \text{ mg}$   
109  $\text{L}^{-1}$ . Because this area is under consideration for future urban development,  
110 remediation of both the vadose zone and groundwater there is of major concern.

111 The stratigraphy of the area is characterized by Neogene and Pleistocene sediments,  
112 mainly of sands and sandstones with interbedding of clay lenses (Gvirtzman, 2002).  
113 The vadose zone lithological profile at the site was assessed again through a borehole  
114 that was drilled at the pilot site in 2012 (Table 1, Fig. 1). Most of the profile is  
115 composed of yellow and red sand layers with low clay content ( $<5 \%$ ), with interbeds  
116 of brown sand containing variable clay content of up to  $11 \%$ . A single  $\sim 1\text{m}$  thick clay  
117 layer ( $27.5 \%$  clay content) was observed at a depth of  $13.3 \text{ m}$ . To improve infiltration  
118 capacity in deep sections of the vadose zone during the remediation experiment, a  
119 shallow clay layer with low permeability, known as “nazaz” (Singer, 2007), was  
120 removed from a depth of  $2.5\text{--}3 \text{ m}$  by excavation. The excavated area,  $10 \times 30 \text{ m}$ ,

121 which was primarily assigned for the pilot infiltration experiment, was backfilled with  
122 the sandy loam from the excavated site after removal of the 0.5m thick nazaz layer.  
123 This layer is therefore presented in the profile as disturbed soil.

124 The climate in the area is characterized as subtropical Mediterranean with a hot and  
125 dry summer from May to October and a colder wet winter from November to April.  
126 The average air temperature on summer and winter days is 30 °C and 17 °C,  
127 respectively. The average annual precipitation is 530 mm year<sup>-1</sup>, mostly as rain  
128 occurring mainly in four to seven rainy episodes during the winter season (IMS,  
129 2011).

### 130 **3 Experimental setup**

#### 131 **3.1 Vadose-zone monitoring setup**

132 Real-time characterization of flow and transport processes in the vadose zone, as well  
133 as assessment of chemical transformation of the percolating water during the  
134 remediation experiments were carried out with a VMS that was installed across the  
135 entire unsaturated profile, from land surface to a depth of 37 m (Fig. 2). A detailed  
136 description of the VMS, its structure, installation procedure and performance, can be  
137 found in previous publications (Dahan et al., 2009; Rimon et al., 2011a) and in the  
138 supplementary material. In particular, the VMS that was used at this site was  
139 composed of a 44m long flexible polyurethane sleeve hosting 11 monitoring units  
140 distributed along its length. Each monitoring unit included: (a) a flexible time-domain  
141 reflectometer (FTDR) sensor for continuous measurement of variations in the  
142 sediment water content (Dahan et al., 2008; Rimon et al., 2007), and (b) vadose-zone  
143 sampling ports (VSPs), which enable frequent sampling of the vadose zone pore water  
144 for chemical analysis (Baram et al., 2012a; Dahan et al., 2009; Rimon et al., 2011b;

145 Turkeltaub et al., 2016). The VMS flexible sleeve was installed in a 0.16m diameter  
146 uncased borehole drilled slanted at a 55° angle (to the horizon) to a vertical depth of  
147 37 m. In addition to the 11 monitoring units that were installed with the VMS, four  
148 additional monitoring units were installed directly in the soil at depths of 0.5 m and  
149 1.5 m. It should be noted that the slanted installation is preferred to ensure that  
150 measurements carried out by each monitoring unit take place in separate undisturbed  
151 sediment columns. In addition, the flexibility of the monitoring sleeve and its filling  
152 with non-shrinking cement grout ensured complete sealing of the borehole void and  
153 prevention of cross-contamination through preferential flow in the borehole.

### 154 **3.2 Field setup**

155 Water amended with ethanol as the electron donor for perchlorate-reducing bacteria  
156 was infiltrated into the vadose zone through an area of 8 x 30 m at the pilot site using  
157 a drip-irrigation system. Dripping lines with drippers having a nominal discharge rate  
158 of 2.2 L h<sup>-1</sup> were set up in a 0.3 x 0.3 m spatial distribution to create fairly even water  
159 distribution over the area. Accordingly, the total discharge rate of the irrigation  
160 system was set to 5 m<sup>3</sup> h<sup>-1</sup>, which is equivalent to an infiltration rate of 0.02 m h<sup>-1</sup>. To  
161 promote anaerobic conditions in the unsaturated zone, a polyethylene liner covered  
162 with soil was placed over the dripper system after its installation. Ethanol was  
163 selected as the electron donor and carbon substrate because it is a natural, soluble  
164 compound that is commonly used by perchlorate-reducing bacteria (Bardiya and Bae,  
165 2011). Moreover, it reduce potential increase in soil salinity associated with other  
166 common sources of electron donors such as acetate (Gal et al., 2008).

### 167 **3.3 Infiltration experiments**

168 Three infiltration experiments with variable amounts of water and ethanol were  
169 implemented at the pilot site over a period of 7 months. To trace the percolating water  
170 across the unsaturated zone, bromide (as KBr) was added to the infiltrating water at  
171 the early stages of the experiment. The infiltration rates, as well as the concentrations  
172 and application sequence were assigned for each experiment with insight gained from  
173 the previous experiment (Table 2). Accordingly, information obtained by the VMS on  
174 depth propagation of the ethanol and tracer and variations in perchlorate and chloride  
175 concentrations across the unsaturated zone during and after each infiltration  
176 experiment were used to adjust the infiltration procedure in the following stage.

177 The first experiment (8 Aug 2010) consisted of infiltration of 50 m<sup>3</sup> water (equivalent  
178 to 210 mm) (Table 2). The first 6 m<sup>3</sup> were applied as untraced fresh water with no  
179 ethanol to wet the topsoil. This wetting stage is essential to promoting deep transport  
180 and preventing accumulation of tracers and ethanol in the low-flow zone located on  
181 the margins of the dripper's influential zone. Following the initial wetting phase, 0.4  
182 m<sup>3</sup> of bromide tracer solution (as KBr) at a concentration of 12.5 g L<sup>-1</sup> was applied,  
183 followed by 1 m<sup>3</sup> of water with 5 % ethanol. Immediately after the application of the  
184 carbon and tracer solution, the rest of the water (42.6 m<sup>3</sup>) was applied to enhance  
185 transport of the ethanol and tracers to deeper parts of the vadose zone.

186 After obtaining the results pertaining to the wetting process, as well as tracer and  
187 ethanol migration in the vadose zone during the first infiltration experiment, a second  
188 experiment was performed (1 Sep 2010). This experiment was conducted with 100 m<sup>3</sup>  
189 of water (equivalent to 420 mm). Here the first 7 m<sup>3</sup> of water was injected into the  
190 topsoil as untraced fresh water, followed by 1 m<sup>3</sup> of water with 5 % ethanol, and then  
191 the rest of the water dose (92 m<sup>3</sup>). No tracers were used in this experiment. The



192 amount of water used after application of the ethanol was doubled to enhance  
193 migration of the ethanol to deep sections of the unsaturated zone.

194 Results from the first two experiments indicated limited migration of tracer and  
195 ethanol to deeper parts of the vadose zone. A third infiltration experiment was  
196 therefore conducted 5 months later with increased discharge of 300 m<sup>3</sup> (equivalent to  
197 1250 mm). This experiment started with 24 m<sup>3</sup> of untraced water followed by 0.4 m<sup>3</sup>  
198 concentrated (50 %) ethanol solution. Then, the rest of the water (275.6 m<sup>3</sup>) was used  
199 to push the ethanol down into the vadose zone. The large quantity of water applied  
200 after the concentrated ethanol solution was designed to enhance quick migration of  
201 the ethanol to deep parts of the vadose zone while minimizing its biodegradation in  
202 the upper soil layers.

### 203 **3.4 Analytical procedure**

204 Perchlorate was analyzed with a perchlorate ion-selective electrode (ISE; Laboratory  
205 Perchlorate Ion Electrode, Cole-Parmer, USA). All samples measured with the ISE  
206 were adjusted by dilution to a concentration range of 10–100 mg L<sup>-1</sup>. Duplicates were  
207 frequently analyzed by injecting 25 µL sample into a Thermo Scientific™ Dionex™  
208 ion chromatography system (ICS 5000) equipped with Ion Pac AS19 column  
209 (detection limit of ±0.01 mg L<sup>-1</sup>). Because results from the two methods were not  
210 significantly different, most of the data reported here are from the perchlorate  
211 electrode with a detection limit of 1 ppm. Bromide and chloride were analyzed by ion  
212 chromatography with a detection limit of 30 ppb (Gal et al. 2008). Total organic  
213 carbon (TOC) was analyzed to examine the success of delivering carbon to the vadose  
214 zone. Because porewater samples from the vadose zone are obtained through the VSP,  
215 which uses a porous ceramic interface (pore size < 2 µm), TOC values reflect DOC.

216 TOC was analyzed through a combustion TOC analyzer (Teledyne Tekmar, Apollo  
217 9000) with a detection limit of 2 ppm. Ethanol concentration in the vadose zone pore  
218 water was analyzed in a gas chromatograph (Varian, CP3800). Water samples (1.5  
219  $\mu\text{L}$ ) were injected by autosampler. The FID and injector temperatures were set to 270  
220 and 250  $^{\circ}\text{C}$ , respectively. The GC oven temperature was first held at 50  $^{\circ}\text{C}$  for 1 min,  
221 increased to 220  $^{\circ}\text{C}$  at a rate of 25  $^{\circ}\text{C min}^{-1}$ , and then held for 4 min. The separation  
222 was performed by Stabilwax<sup>®</sup> capillary column (60 m, 0.32 mm, 0.25  $\mu\text{m}$ , Restek  
223 Corporation, USA); helium was used as the carrier gas (1  $\text{mL min}^{-1}$ ). For  
224 quantification, five external standards were used.

#### 225 **4 Results and discussion**

226 All of the data obtained by the VMS are presented here as variations in measured  
227 parameters with depth, as commonly done to describe depth profiles. However, to  
228 ensure measurements under undisturbed vertical profiles, the VMS was installed in a  
229 slanted orientation (Fig. 2 and supplementary material). Thus, each monitoring unit  
230 faces an undisturbed profile that is shifted horizontally and vertically from the other  
231 units. Accordingly, although the data are presented as depth profiles, they should be  
232 regarded as individual points distributed across the 3D space of the vadose zone  
233 (Dahan et al., 2007; Rimon et al., 2011a).

234 Prior to detailed discussion on the results a general outline of the rationale behind the  
235 experimental setup will be presented here. Three infiltration experiments were  
236 conducted with variable amounts of water, ethanol as electron donor, and bromide as  
237 a tracer (all of which is presented above in chapter 3.3 *Infiltration experiment*).  
238 Nevertheless, the experimental conditions in each experiment were set following the  
239 results obtained from the previous stage. The first infiltration experiment was

240 conducted as a first trial to infiltrate ethanol-enriched water-solution into the  
241 unsaturated zone. This experiment was also conducted with bromide as a tracer in  
242 order to mark the water front propagation across the unsaturated zone. As will be  
243 discussed further on, results the first infiltration experiment indicated that the  
244 migration capacity of both ethanol and bromide across the unsaturated profile was  
245 very limited. Accordingly a second infiltration experiment was conducted with a  
246 double amount of water and the same amount and concentration of ethanol in order to  
247 enhanced deep migration of the ethanol down the unsaturated zone. Following the  
248 results from the first two experiments a third infiltration experiment was conducted  
249 with larger water volumes and higher ethanol concentration in order to avoid quick  
250 ethanol degradation in the shallow soil. all of which will be presented and discussed  
251 below.

#### 252 **4.1 Water percolation**

253 Temporal variations in the vadose zone water content provide a direct indication of  
254 percolation processes in the vadose zone (Rimon et al., 2007; Dahan et al., 2008;  
255 Turkeltaub et al., 2015). Each infiltration experiment launched a wetting wave that  
256 propagated sequentially through the unsaturated zone (Fig. 3). Down-migration of the  
257 wetting wave was expressed as a quick rise in water content followed by a recession  
258 caused by water redistribution and drainage. Referring the wetting sequence in the  
259 vadose zone to the infiltration events on land surface enabled a direct calculation of  
260 the flow velocity across the unsaturated zone (Rimon et al., 2007; Dahan et al., 2008).  
261 All three infiltration experiments produced wetting fronts that moved down the  
262 vadose zone at a velocity of  $\sim 0.18 \text{ m h}^{-1}$ , even though the water volumes that were  
263 used in each experiment were significantly different (50, 100 and  $300 \text{ m}^3$ ). Additional

264 information on calculation procedure of flow velocities may be found in to  
265 supplementary material. Observations of regulated flow velocities at constant rates  
266 across the vadose zone under variable surface hydraulic conditions have also been  
267 reported in other studies (Dahan et al., 2008; Amiaz et al., 2011; Rimon et al., 2011a).

268 The high salinity of the deeper parts of the vadose zone (>13 m) (Fig. 1) limits the  
269 reliability of the TDR technology for measuring water content at those depths (Nadler  
270 et al., 1999). Therefore, variation in water content, as an indication of deep  
271 percolation, is presented here only down to a depth of 11.2 m, where the salinity was  
272 low enough to achieve reliable moisture measurements with the FTDR sensors.  
273 Nevertheless, indications of deep percolation in the deeper layers (>13 m) are further  
274 discussed through the variation in chemical composition of the percolating water  
275 across the entire thickness of the unsaturated zone (40 m).

#### 276 **4.2 Perchlorate transformation and mobilization**

277 Initial analysis of porewater samples from the vadose zone, prior to initiation of the  
278 infiltration experiments, revealed very high concentrations of perchlorate and  
279 chloride, both reaching maximum values of  $\sim 22,500 \text{ mg L}^{-1}$  (Fig. 1), and total  
280 dissolved solids (TDS) of  $43,000 \text{ mg L}^{-1}$ , at a depth of 21 m. Note that at this stage,  
281 the concentrations of perchlorate and chloride are nearly identical throughout the  
282 entire profile. These high concentrations, sampled by the VMS, are in accordance  
283 with concentration profiles obtained previously in extracts of sediment samples (Gal  
284 et al., 2009).

285 Frequent sampling of the vadose zone pore water showed dynamic variations in  
286 perchlorate concentration during the percolation experiments. In the upper section of  
287 the vadose zone (0–13 m), perchlorate concentrations decreased dramatically, from as

288 high as 9000 mg L<sup>-1</sup> to below detection levels (Fig. 4). Such a reduction in  
289 concentration in a relatively thick portion of the vadose zone (13 m) over the short  
290 period of 10 months is clearly desirable and may even be considered a great success.  
291 Nevertheless, closer inspection of the variations in perchlorate concentration in deep  
292 parts of the vadose zone (17–40 m) showed an increase at most of the measurement  
293 points (Fig. 5). Perchlorate concentration rose from 12,700 mg L<sup>-1</sup> to 27,400 mg L<sup>-1</sup> at  
294 a depth of 17 m during the same period. A similar increase in concentration was also  
295 found in deeper parts of the cross section at depths of 25, 28, and 36 m. Note that  
296 during this period, an increase in perchlorate concentration was even observed in the  
297 groundwater (represented at a depth of 41 m in Fig. 5). Obviously, the mixed trend in  
298 variations of perchlorate concentration implies that transformation and mobilization  
299 processes take place simultaneously. As such, the conditions for both biodegradation  
300 and mobilization should be examined along with the variation in perchlorate  
301 concentration.

### 302 **4.3 Electron donor availability**

303 Available organic carbon as an electron donor is crucial for perchlorate reduction. To  
304 increase the concentration of DOC in the vadose zone, ethanol was mixed with the  
305 percolating water during the early stage of each infiltration experiment. Analysis of  
306 ethanol and DOC in the water samples from the vadose zone throughout the  
307 experiment revealed high correlation between the two. Theoretically one gram per  
308 liter of ethanol is equal 0.52 gram per liter of soluble carbon. However, in the site the  
309 dissolved carbon composes of ethanol its oxidation products (such as acetate) as well  
310 as other soluble microbial metabolites that can also serve as electron donors. Thus,  
311 DOC provides a better knowledge on the availability of electron donors in the soil  
312 pore water. Accordingly, we assume that the variation in DOC during the experiments  
313 was due to transport of ethanol or ethanol-degradation products with the percolating

314 water (for further details correlation between DOC and ethanol concentration see  
315 supplementary material).

316 During the first infiltration experiment, an increase in DOC above background levels  
317 was observed only at shallow depths, down to 1.5 m (Fig. 6). No signs of increasing  
318 DOC were observed in the deeper parts of the cross section at this stage. Twenty-three  
319 days later, before initiation of the second infiltration experiment, DOC values had  
320 dropped back down to background levels. This implies that the ethanol was  
321 microbiologically consumed and mineralized to inorganic carbon in the soil before it  
322 could be leached further down.

323 As a result of the limited transport of electron donor, ethanol, in the first infiltration  
324 experiment, a second experiment was conducted with the same mass and  
325 concentration of ethanol. However, it was flushed with double the amount of water to  
326 promote its quicker migration to deeper layers (Fig. 4). In this experiment, no signs of  
327 increasing DOC were observed at any depth. On the contrary, DOC level decreased to  
328 values below background levels (Fig. 6). Obviously, the rate of ethanol metabolism  
329 and mineralization in the soil increased following the first experiment, where both  
330 water content of the sediment and substrate required for efficient microbial activity  
331 increased. As a result, ethanol-degradation efficiency in the topsoil (<0.5 m) was  
332 significantly enhanced.

333 To overcome the limitation of electron donor delivery through the shallow soils, a  
334 third infiltration experiment was designed. In this experiment, the ethanol was  
335 injected in a 0.4m<sup>3</sup> high-concentration (50 % volume percentages) pulse followed by a  
336 large volume of water. Application of ethanol at a very high concentration was aimed  
337 at suppressing its biological degradation in the shallow soil. The ethanol pulse was  
338 introduced after application of 24 m<sup>3</sup>, the latter to provide high initial wetting

339 conditions under the ethanol front. Then the ethanol slug was pushed down with 276  
340 m<sup>3</sup> of water. At this stage of the study, which was conducted 6 months after the  
341 previous one, a substantial increase in DOC was observed in the entire top 13 m of the  
342 cross section (Fig. 6). Obviously, an increase in DOC serving as electron donor is an  
343 essential prerequisite for perchlorate degradation. Apparently, application of ethanol  
344 at a high concentration, which inhibited its degradation in the upper layer, succeeded  
345 to drive the ethanol all the way down to 13 m, just above the clay layer. Nevertheless,  
346 no signs of DOC increase were observed below 13 m.

#### 347 **4.4 Transport and degradation**

348 The mechanism controlling down-propagation of a non-conservative substance such  
349 as ethanol may be elucidated by looking at the migration pattern of a conservative  
350 tracer such as bromide. Bromide was injected with the percolating water in the early  
351 stages of the first infiltration experiment. Results on bromide migration are presented  
352 here only for the top 13 m, where the background concentrations prior to the initiation  
353 of the infiltration experiment were below detection limits. Concentration profiles  
354 during the infiltration experiments clearly demonstrated sequential progress of the  
355 percolating water across the top 13 m of the unsaturated zone (Fig. 7). Mass balance  
356 calculation of bromide on the basis of the concentration profiles (Fig. 7) and sediment  
357 water content (Fig. 3) on various dates after the infiltration experiment resulted in  
358 high recovery rates of 85–127 %. A comparison of the transport patterns of bromide  
359 and DOC confirmed that biodegradable material such as ethanol is rapidly consumed  
360 in the vadose zone.

361 An increase in chloride concentration in the vadose zone is usually attributed to  
362 evaporation processes near land surface, a mechanism that is unlikely to occur in this

363 particular setup where the surface is isolated from the atmosphere. Accordingly,  
364 variations in chloride concentration across the vadose zone may be attributed to  
365 chloride mobilization with the percolating water and perchlorate reduction. Therefore,  
366 degradation of perchlorate is expected to result in an increase in chloride mass.

367 Prior to the infiltration experiments, chloride-to-perchlorate ratios in the vadose zone  
368 were very similar, exhibiting nearly identical profiles (Fig. 1) with equivalent  
369 concentration proportions of 2.4–5.5 (Fig. 8). Following the infiltration experiment, a  
370 significant increase in ionic ratios was observed in the top 13 m, while in the rest of  
371 the profile—from a depth of 17 m to the water table, the concentration ratio of  
372 chloride to perchlorate remained relatively unchanged. Obviously, since both  
373 perchlorate and chloride are very soluble and mobile, infiltration water with a low  
374 concentration of chloride ( $\sim 100 \text{ mg L}^{-1}$ ) and zero perchlorate is also expected to result  
375 in an increased chloride-to-perchlorate ratio, even if no perchlorate degradation takes  
376 place. Since both chloride and perchlorate are very mobile and easily displaced with  
377 the percolating water, quantification of the perchlorate-degradation rate with respect  
378 to its down-leaching is not straightforward.

## 379 **5 Conclusions**

380 The infiltration experiments were primarily aimed at improving the environmental  
381 conditions for perchlorate-reducing bacteria across the vadose zone. This included an  
382 increase in water content along the soil profile and amendment of the electron donor.  
383 The results, which were based on continuous monitoring of the entire vadose zone,  
384 exhibited notable variation in the concentrations of perchlorate, DOC and other  
385 solutes in the unsaturated zone. Increased concentrations of DOC with a concurrent  
386 reduction in perchlorate concentration (from thousands to a few milligrams per liter)



387 and increased chloride-to-perchlorate ratio (from ~2.5 to ~300) in the upper 13 m  
388 indicated that perchlorate is partially reduced in this part of the vadose zone. On the  
389 other hand, no evidence of improved reducing conditions was observed in the deeper  
390 parts, where the initial concentrations of perchlorate were significantly higher.  
391 Nevertheless, since assessment of redox conditions in deep vadose zone is not yet  
392 feasible, we can only rely on variations in the chemical composition to assess the  
393 existence of degradative conditions.

394 The limited ability to deliver a soluble electron donor across a microbiologically  
395 reactive medium, such as topsoil, is a major limiting factor for remediation of the  
396 deep vadose zone through gravitational percolation of enriched solution. Note that  
397 temporal variations in the concentrations of perchlorate, as well as other solutes, in the  
398 deep parts of the vadose zone, i.e., under the clay layer at 14 m, indicate that the clay  
399 layer does not play any role in limiting infiltration capacity in terms of flow velocity  
400 and fluxes. Similar observations on the role of clay layers in infiltration in the  
401 unsaturated zone have been reported in previous publications (Baram et al., 2012b,  
402 2012c; Dahan et al., 2009; Rimon et al., 2007; Turkeltaub et al., 2015b).

403 The attempts to leach the ethanol down into the vadose zone with large quantities of  
404 water inevitably drove down-leaching and displacement of the dissolved solutes,  
405 including perchlorate. Although there were indications of partial degradation of  
406 perchlorate in the upper part of the vadose zone, its downward displacement toward  
407 the water table was evident from the sequential increase in perchlorate concentration  
408 with depth (Fig. 5). It seems that the entire column of perchlorate mass was pushed  
409 down by the percolating water toward the water table, which also resulted in an

410 increased concentration of perchlorate in the observation well, which was located  
411 under the infiltration zone.

412 Enhancing biodegradation of contaminants in the vadose zone while minimizing their  
413 down migration into groundwater is a major challenge in remediation operations that  
414 involves water infiltration. Although in this study we have observed dramatic  
415 reduction in perchlorate concentration in the top 13 m of the unsaturated zone  
416 following the infiltration of ethanol enriched water solution, we can't state that the  
417 reduction in perchlorate concentration is only due to bio-degradation and exclude  
418 partial down leached to deeper parts of the vadose zone. Accordingly, perchlorate  
419 degradation vs. migration process were investigated through the temporal variation in  
420 perchlorate concentration with respect to variations in concentrations of ethanol,  
421 which was consumed in the subsurface, Br, which is conservative tracer, and  
422 variations in the chloride concentration, which is perchlorate final degradation  
423 product. All of which provided indicator hints to the question on the degradation vs  
424 leaching.

425 The study demonstrates that application of vadose-zone monitoring technology during  
426 a remediation operation provides real-time information on the chemical and  
427 hydrological state of the subsurface. Linking the temporal variation in the chemical  
428 composition of the vadose zone pore water, sediment saturation degree and flow  
429 velocities are vital for efficient management of remediation operations.

430 *Author contribution:* Ofer Dahan (PI, Vadose zone hydrology) design of the  
431 experimental and monitoring setup. Idan Katz (MSc student) conducted the field  
432 experiment and laboratory analysis. Lior Avishai (MSc student) conducted data  
433 analysis and modeling of flow and transport in the unsaturated zone. Zeev Ronen (PI,

434 *Microbiology) design the bio treatment setup. Data analysis and manuscript*  
435 *preparation - all coauthors.*

436 ***Competing interest:*** *The authors declare that they have no conflict of interest.*

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439

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- 590

591 *Table 1. Sedimentological Composition of the Vadose Zone at the Pilot Site*  
 592

Depth (m)	Description	Clay Content (%)
0-3	Red sand (disturbed)	7.5
3-5	Red sand (Hamra)	5
5-7	Red-yellowish sand	5
7-10	Yellow sand	5
10-13	Brown sand	5
13-14	Dark brown clay	27.5
14-17	Red-brown clayish sand	12.5
17-20	Brown clayish sand	3.75
20-27	Yellow sand	1
28-29	Brown sand	11.75
29-33	Red-clayish sand (Hamra)	3
33-41	Yellow sand	0

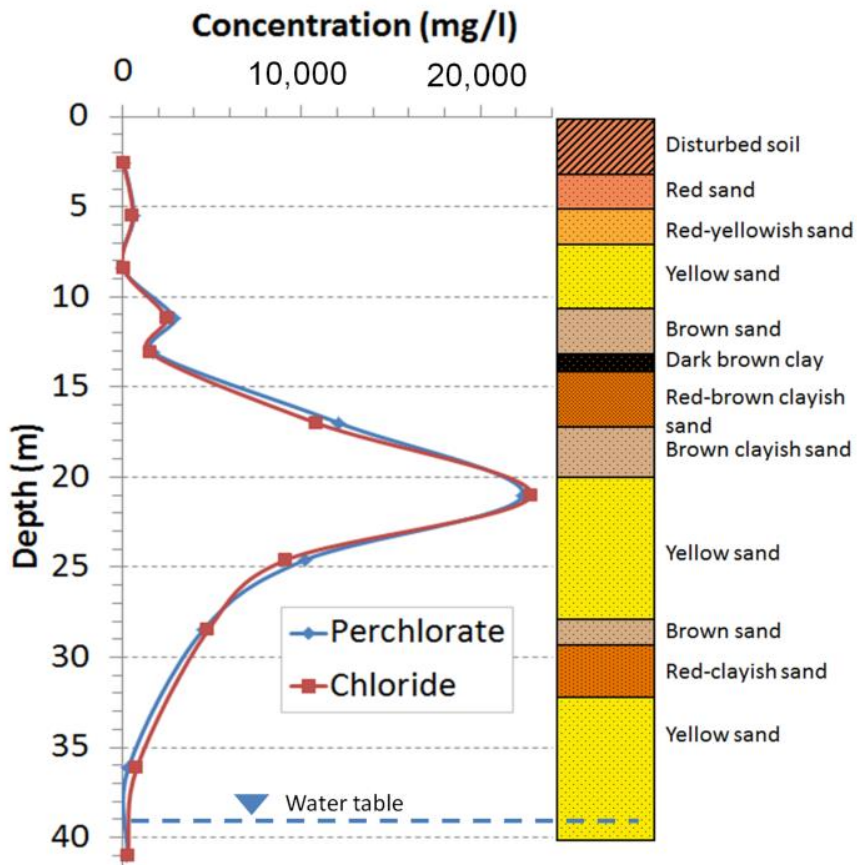
601  
 602 *Table 2. Infiltration experiment conditions*

Date	Water Volume (m <sup>3</sup> )	Equivalent Water Depth (mm)	Ethanol (l)	Bromide (Kg)
8 Aug 2010	50	210	50	5
1 Sep 2010	100	420	50	-
27 Feb 2011	300	1250	200	-

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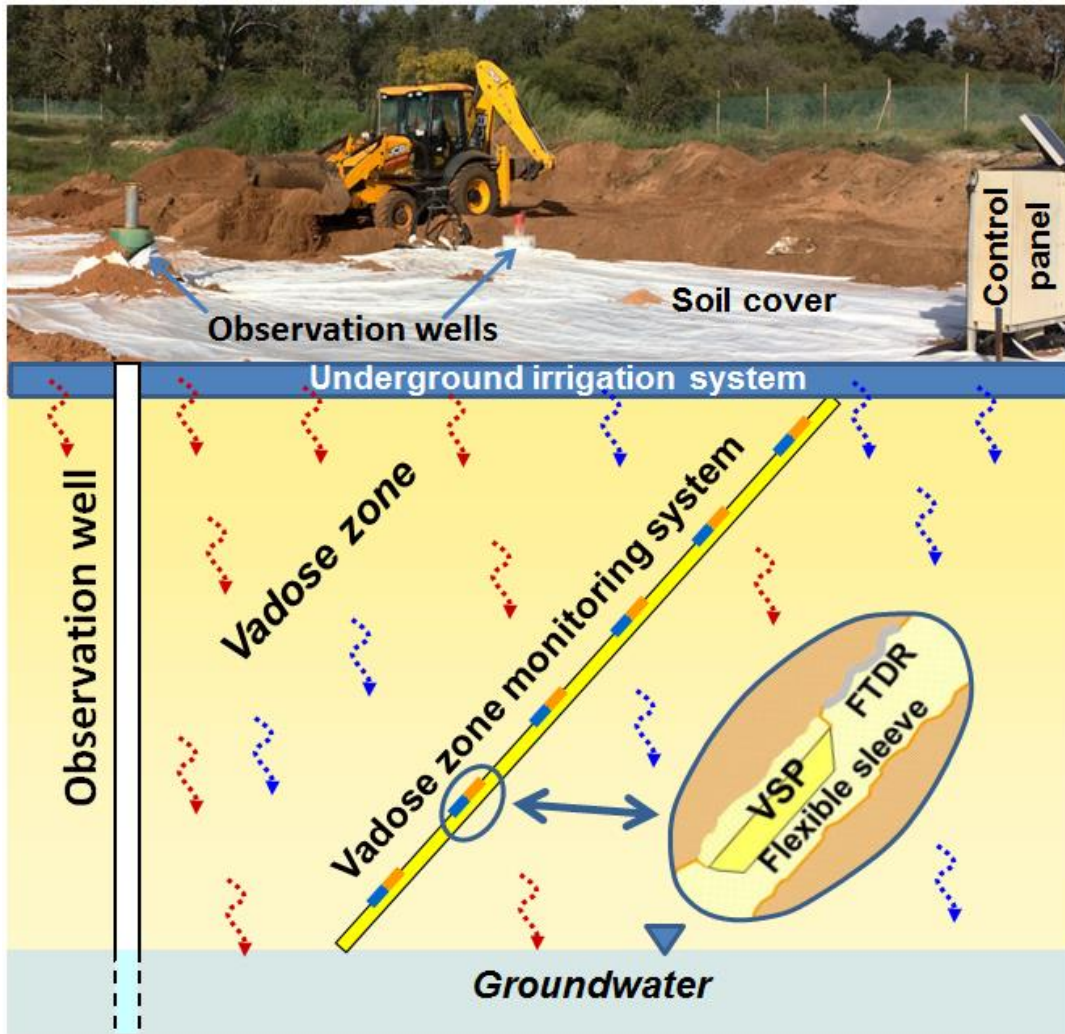




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606 Figure 1. Initial concentration profiles of chloride and perchlorate in the vadose zone  
 607 pore water under the former waste lagoon, along with the lithological profile.

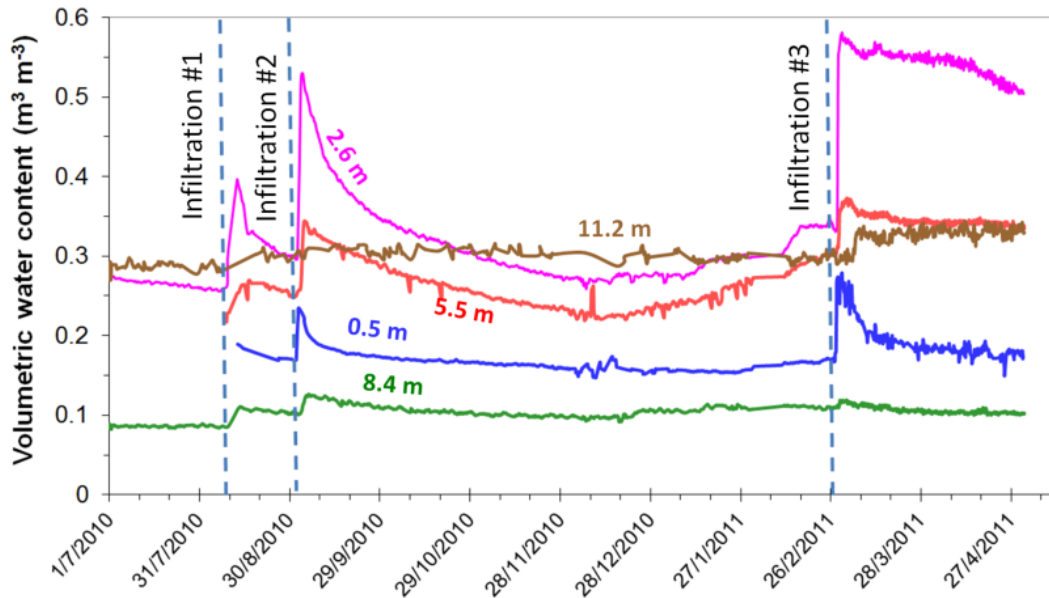
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610 Figure 2. Schematic illustration of the vadose-zone monitoring system installed in the  
 611 vadose zone under the infiltration pilot site. In the picture above the vadose zone, the  
 612 irrigation system at the site is being covered.

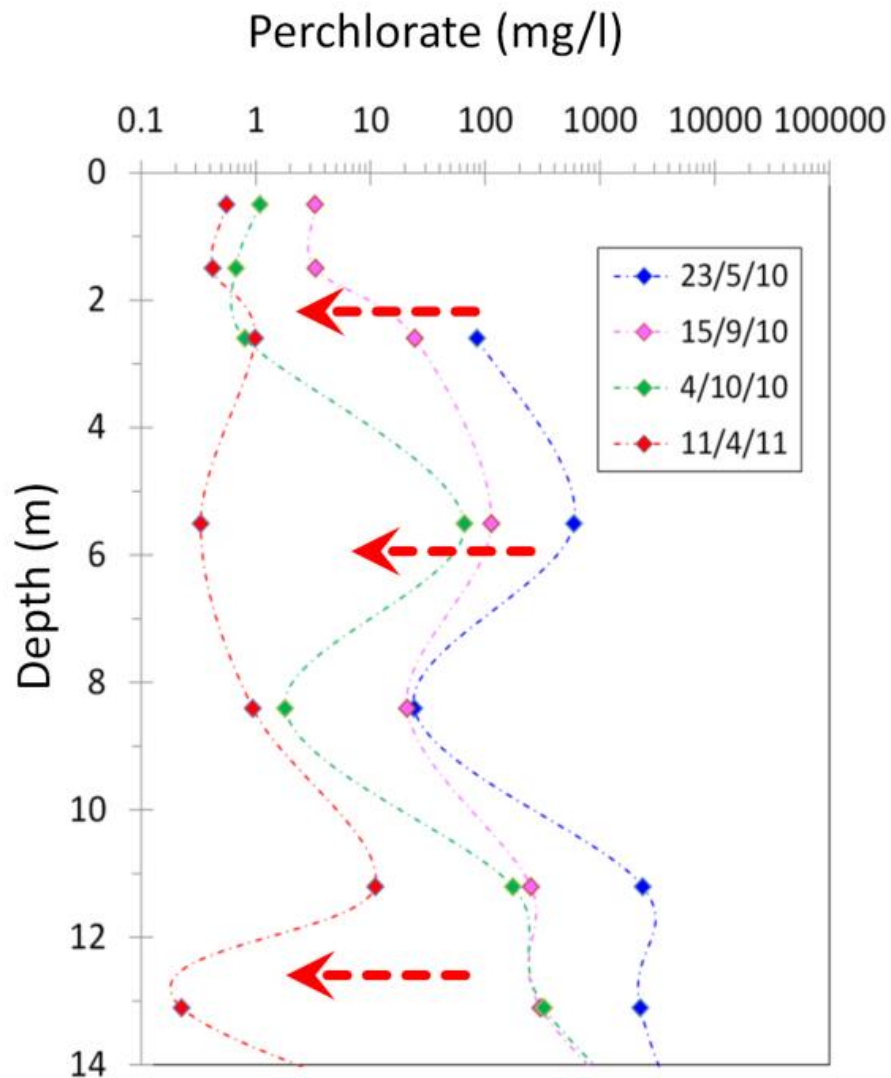
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615 Figure 3. Temporal variations in sediment water content in the top 13 m of the vadose  
 616 zone during the infiltration experiments. Dates are given as day/month/year.

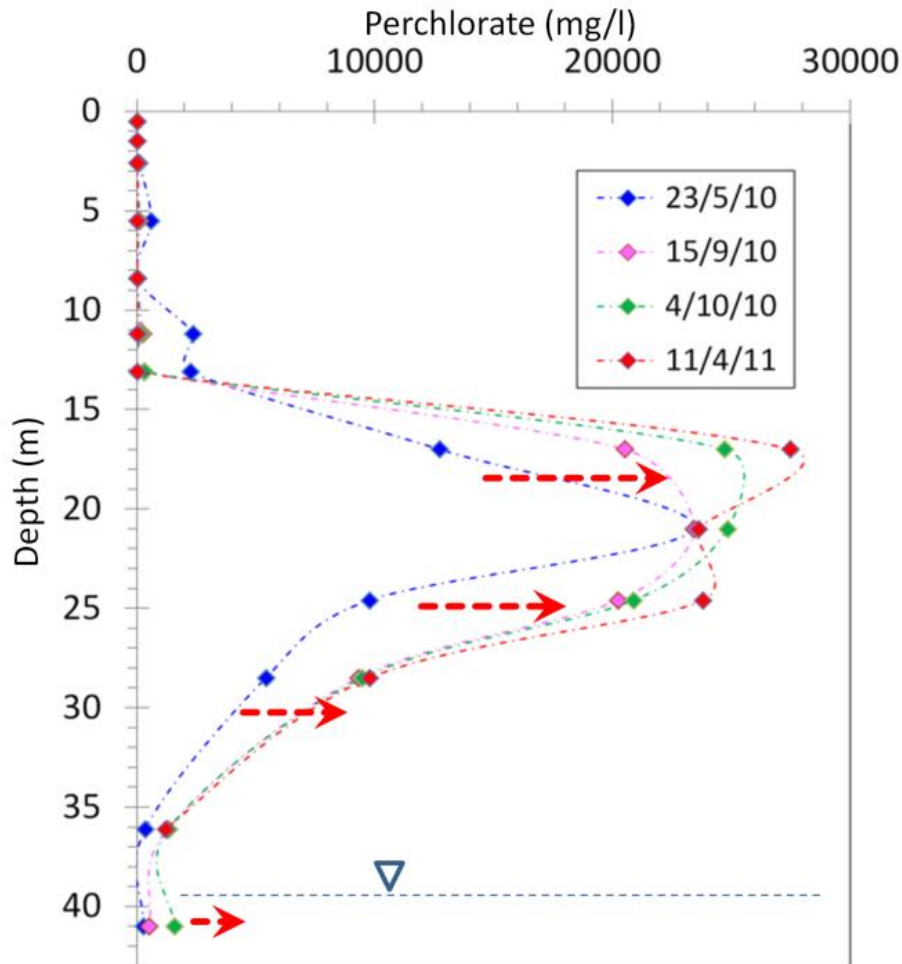
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619 Figure 4. Perchlorate concentration profile across the top 13 m of the vadose zone  
 620 under the pilot site during the infiltration experiments. The profiles emphasize the  
 621 gradual decrease in perchlorate concentration with time (marked in red arrows). Dates  
 622 are given as day/month/year. Note that data points are aligned in a slanted orientation  
 623 and interpolated as time intervals.

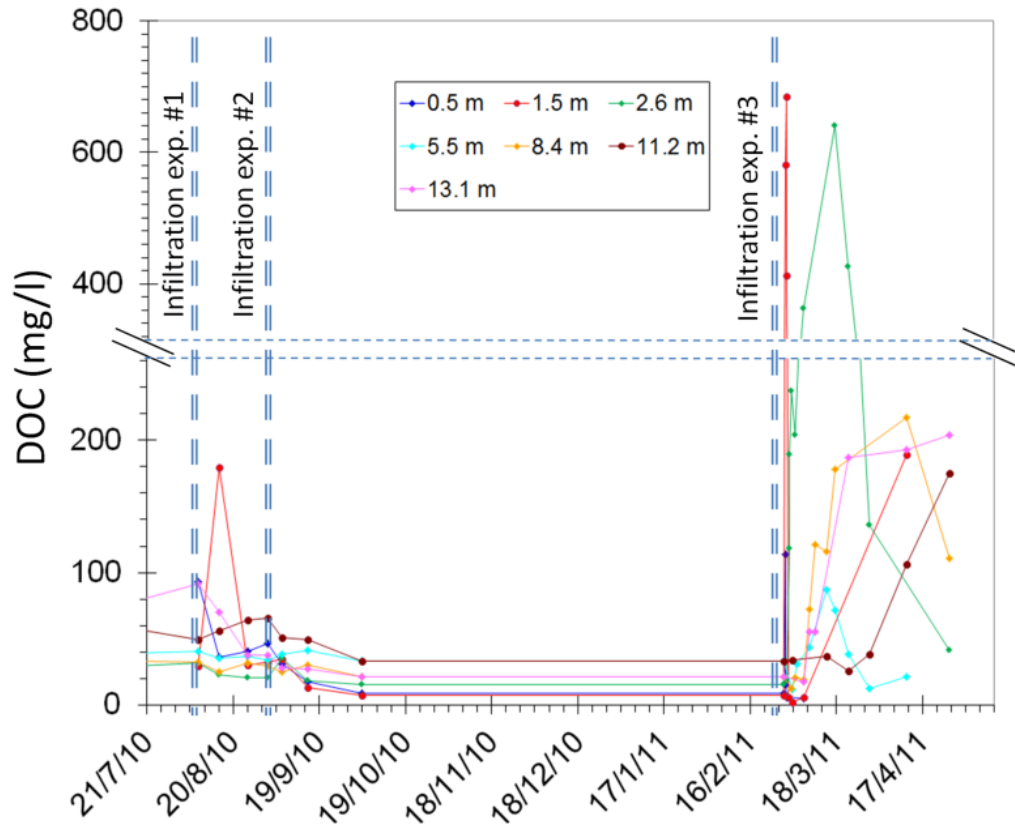
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626 Figure 5. Perchlorate concentration profile across the entire vadose zone and top  
 627 groundwater under the pilot site during the infiltration experiments. The profiles  
 628 emphasize the gradual increase in perchlorate concentration with time (marked in red  
 629 arrows). Dates are given as day/month/year. Note that data points are aligned in a  
 630 slanted orientation and interpolated as time intervals.

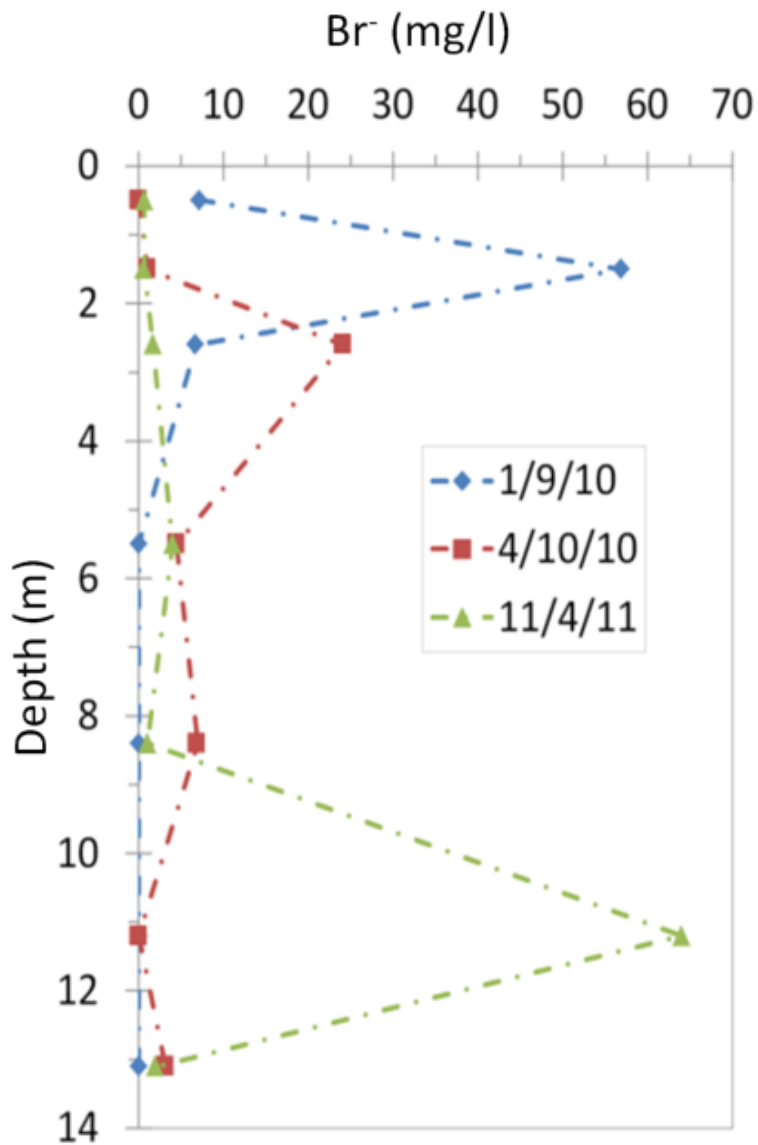
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633 Figure 6. Variations in dissolved organic carbon (DOC) across the top 13 m of the  
 634 vadose zone following infiltration of water enriched with ethanol. Dates are given as  
 635 day/month/year.

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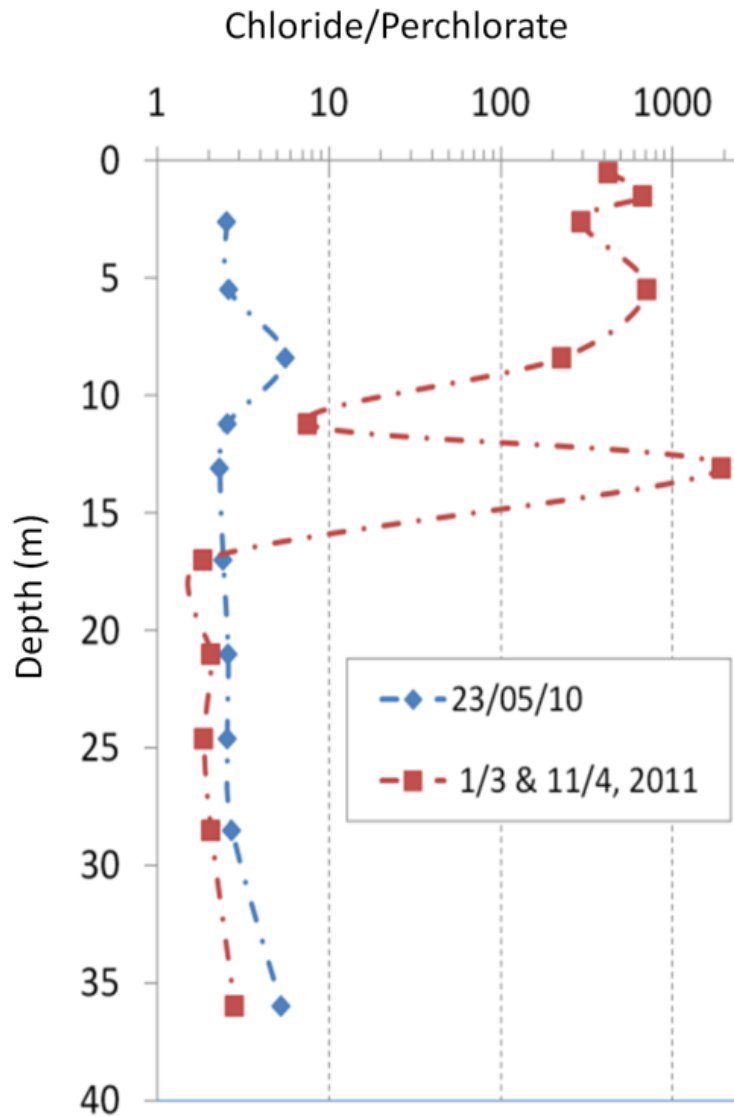


637

638 Figure 7. Variations in bromide concentration profile across the top 13 m of the  
 639 vadose zone during the infiltration experiments. Dates are given as day/month/year.

640 Note that data points are aligned in a slanted orientation and interpolated as time  
 641 intervals.

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644 Figure 8. Chloride-to-perchlorate equivalent concentration ratio profiles before and  
 645 after the infiltration experiments. Dates are given as day/month/year. Note that data  
 646 points are aligned in a slanted orientation and interpolated as time intervals.

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