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Persistence of Artificial Sweeteners

in a

15-Year-Old Septic System Plume

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23 **Abstract**

24 Groundwater contamination from constituents such as NO_3^-, often occurs where multiple

25 sources are present making source identification difficult. This study examines a suite of

26 major ions and trace organic constituents within a well defined septic system plume in

27 southern Ontario, Canada (Long Point site) for their potential use as wastewater tracers.

28 The septic system has been operating for 20 years servicing a large, seasonal-use

29 campground and tritium/helium age dating indicates that the 200 m long monitored

30 section of the plume is about 15 years old. Four parameters are elevated along the entire

31 length of the plume as follows; the mean electrical conductivity value (EC) in the distal

32 plume zone is 926 µS/cm which is 74% of the mean value below the tile bed, Na^+ (14.7

33 mg/L) is 43%, an artificial sweetener, acesulfame (12.1 µg/L) is 23% and Cl^- (71.5 mg/L)

34 is 137%. EC and Cl^- appear to be affected by dispersive dilution with overlying

35 background groundwater that has lower EC but has locally higher Cl^- as result of the use

36 of a dust suppressant ($CaCl_2$) in the campground. Na, in addition to advective dilution,

37 could be depleted by weak adsorption. Acesulfame, in addition to the above processes

38 could be influenced by increasing consumer use in recent years. Nonetheless, both Na^+

39 and acesulfame remain elevated throughout the plume by factors of more than 100 and

40 1000 respectively compared to background levels, and are strong indicators of

41 wastewater impact at this site. EC and Cl^- are less useful because their contrast with

42 background values is much less (EC) or because other sources are present (Cl^-). Nutrients

43 (NO_3^-, NH_4^+, PO_4^{3-}, K^+) and pathogens (E. coli) do not persist in the distal plume zone

44 and are less useful as wastewater indicators here. The artificial sweetener, acesulfame,

45 has persisted at high concentrations in the Long Point plume for at least 15 years (and this

46   timing agrees with tritium/helium-3 dating) and this compound likely occurs at uniquely

47   high concentrations in domestic wastewater. As such, it holds considerable promise as a

48   powerful new tracer of wastewater impact in groundwater.

49

50   **Introduction**

51   Groundwater contamination from constituents such as nitrate often occurs where

52   multiple sources are present making source identification difficult. Groundwater

53   impacted by agricultural fertilizer and manure applications often has domestic wastewater

54   disposal occurring in the same area and their compositions can be similar. Also in semi-

55   arid regions such as the US southwest, infiltration basins that use reclaimed wastewater

56   are widely used to augment aquifer recharge. Here there is a need to quantify the fraction

57   of wastewater-sourced groundwater reaching adjacent production wells so that the extent

58   of subsurface renovation can be established (Quast et al., 2006). Thus, there is an interest

59   in identifying constituents that serve as intrinsic tracers of wastewater input. Nutrients

60   and pathogens can be affected by a variety of subsurface immobilization and degradation

61   reactions such as vadose zone immobilation (pathogens), denitrification (NO_3^-),

62   anammox (NO_3^- and NH_4^+) and adsorption (PO_4^{3-} and K^+), making these parameters

63   generally less useful as wastewater indicators. The minor constituent Boron (B) is mobile

64   and persistent in groundwater and is usually elevated in domestic wastewater by a factor

65   of about five (0.3-1 mg/L) compared to background groundwater, as a result of its use in

66   laundry detergents. Wastewater B is also usually isotopically distinct from natural

67   sources (Barth, 1998) and has been used successfully as an intrinsic wastewater tracer in

68   both groundwater (Vengosh et al., 1994; Bassett et al., 1995; Bussey and Walter, 1996)

69   and surface waters (Chatelat and Gaillardet, 2005). However concentration contrasts with

70   background values are relatively small, and wastewater B isotopic signatures can overlap

71   with those of other sources, such as natural B occurring in saline groundwater (Bassett et

72   al., 1995).

73   Some trace organic constituents that are relatively unique to domestic wastewater

74   persist during sewage treatment and have been used successfully as wastewater tracers in

75   both surface waters and groundwater. These include compounds such as carbamazapine

76   and crotamiton found in pharmaceutical and personal care products (Clara et al., 2004;

77   Heberer et al., 2004; Nakada et al., 2008; Sabourin et al., 2010), ibuprofen (Carrara et al.,

78   2008), caffeine (Buerge et al., 2003) and estrogen active compounds (Quanrud et al.,

79   2004).   However, the degree to which these compounds persist in groundwater flow

80   systems over multiyear and decadal timeframes has not yet been well established.

81   More recently, several artificial sweeteners widely used in the food and beverage

82   industry have also been shown to resistant breakdown during sewage treatment and to

83   persist quantitatively in surface water and groundwater environments (Buerge et al.,

84   2009; Van Stempvoort et al., 2011a; Van Stempvoort et al., 2011b). These have also been

85   suggested as potential wastewater tracers, however their longer term persistence in

86   subsurface environments has not yet been established. In this study, our objective was to

87   assess a spectrum of wastewater related parameters within a septic system plume that

88   could be traced over a longer term, multiyear timeframe. The site selected was a large

89   septic system servicing a seasonal use campground at Long Point, ON, Canada, where a

90   well defined groundwater plume is present in an unconfined sand aquifer. Groundwater

91   monitoring in the Tile Bed 2 area (Fig. 1) has been ongoing since it was commissioned in

92   1990 and the fate of a variety of constituents in the groundwater plume have been

93   reported previously including; NO_3^- and NH_4^+ (Aravena and Robertson, 1998; Robertson

94   et al., 2012), PO_4^{3-} (Robertson, 2008); pharmaceutical compounds (Carrara et al., 2008;

95   Sabourin et al., 2010) and the artificial sweeteners, cyclamate, saccharin, sucralose and

96   acesulfame (Van Stempvoort et al., 2011b). Several pharmaceutical compounds including

97   carbamazapene and ibuprofen and several of the sweeteners, particularly acesulfame,

98   which was approved for use in Canada in 1988 (Gougeon et al., 2004), persist in the

99   plume, but the monitoring network used previously only extended 17-25 m from the tile

100   bed and only intercepted the portion of the plume that was about one year old. However,

101   because the septic system is 20 years old, a much longer plume is present at the site. For

102   the current study the groundwater monitoring network was expanded in 2010, by the

103   installation of an additional 23 multilevel, bundle piezometers extending up to 200 m

104   downgradient from the tile bed. Then, on October 27, 2010, a detailed sampling sweep

105   was initiated for a suite of parameters including EC, nutrients (NO_3^-, NH_4^+, PO_4^{3-}), other

106   major ions (Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}), pathogens (E. coli), the four artificial sweeteners

107   and a suite of pharmaceutical compounds, from up to 90 groundwater monitoring points

108   located along the plume centreline and upgradient from the tile bed. This was followed

109   by trace gas sampling at seven monitoring points along the plume in January 2011, to

110   allow tritium/helium ($^3H/^3He$) age dating of the plume. This manuscript reports on the

111   persistence of the major ions and artificial sweeteners in the extended plume and provides

112   a plume age profile. The distribution of the pharmaceutical compounds will be reported

113   in a subsequent manuscript. Additionally, breakthrough behaviour of the major ions and

114   sweeteners at the water table below the tile bed, during the spring 2011 campground start

115   up, is reported.

116

117   **Long Point Site**

118   The Long Point campground located on the north shore of Lake Erie (Fig. 1), has

119   256 overnight campsites and is open seasonally from mid-May until mid-October.

120   Sewage from a single washroom facility is treated on-site, in a conventional septic system

121   consisting of a septic tank and to two separate tile beds (~290 m^2 each) which are

122   intermittently dosed using a float activated pump. Tile Bed 2, which is focus of the

123   current study (Fig. 1), is located on sand where the water table is ~ 2 m deep. Loading to

124   the tile beds was estimated previously at ~10 cm/day during peak loading in the summer

125   (Robertson and Cherry, 1992), which is about 10 times higher than for smaller household

126   septic systems. Water limiting fixtures installed in the washroom in ~2004, result in

127   relatively high concentrations of constituents such as nitrogen (100 mg/L, Table 1) in the

128   wastewater, which is about twice as high as typically occurs in domestic septic tank

129   effluent (e.g. 30-70 mg/L, Hinkle et al., 2008). The plume from Tile Bed 2 flows

130   southward toward the Lake Erie shoreline (Fig. 1) within a ~5 m thick unconfined

131   calcareous sand aquifer which is underlain by a less permeable clayey silt unit.

132   Additional coring undertaken during this study revealed that the contact between the sand

133   and silt units is sharp and is very flat lying throughout the study area (Fig. 2).

134   Groundwater ages in the proximal plume zone were estimated previously from

135   seasonal breakthrough of EC peaks and from two NaBr tracer tests (Robertson et al.,

136   2012) and vary from about seven days in the shallow water table zone below the tile bed

137   (during heavy sewage loading) to about one year, 17 m down gradient from the edge of

138   the tile bed. There is also a strong vertical component of flow below the tile bed (up to

139   ~10 cm/day, Robertson et al., 2012) as a result of the high sewage loading rate.

140   With the exception of the introduction of water limiting fixtures in the washroom

141   in ~2004, which increased concentrations of Cl^- and NH_4^+ in the septic tank effluent by

142   about 50-100% (Table 2), wastewater composition appears to have remained relatively

143   stable over the 20 year operational period (Table 2). The site is thus well suited for

144   examining longer term persistence of potential tracer constituents.

145

146   **Methods**

147   **Monitoring Wells**

148   In the current study, the existing monitoring network of 13 multilevel bundle

149   piezometers (wells 100-140, Fig. 1) was expanded by the installation of an additional 23

150   multilevel bundles in the down gradient area (wells 1-23, Fig. 1). These each consist of

151   from 6-13 variable depth sampling points of 3-6 mm dia. polyethylene tubing with short,

152   5 cm long, slotted and screened tips. Each bundle was installed using direct-push casing,

153   into a single borehole, without the use of filter sand or sealing material. Twenty two of

154   the bundles, with a total of 90 monitoring points, are aligned along section A-A', which

155   follows the centreline of the plume. These include two upgradient bundles (127, 140, Fig.

156   1) which are located within a naturally grassed savannah area that is minimally impacted

157   by anthropogenic activity. Downgradient of the tile bed, the plume migrates under the

158   campground area and precipitation recharge occurring in this area could be affected by a

159   variety of anthropogenic influences such as food and beverage spillage at the campsites

160   and the annual application of a dust suppressant ($CaCl_2$) to the roadways shown on Fig. 1.

161

162   **Plume Sampling and Analyses**

163   Site characterization methods including sediment coring, piezometer installation

164   and groundwater sampling have been described previously (Robertson and Cherry, 1992;

165   Aravena and Robertson, 1998; Robertson, 2008). Most of the data in the current study is

166   from a sampling sweep initiated on October 27, 2010. Much of the sampling was

167   completed on October 27, although infill and repeat sampling continued for up to 30 days

168   thereafter. Additionally, during April-July 2011, time series sampling (n = 12) was

169   undertaken in the shallow water table zone below the tile bed (well 122-2.2 m depth) and

170   from the septic tank effluent (n =10), to observe seasonal breakthrough trends of potential

171   tracer constituents at the water table immediately after the campground was opened for

172   the season on May 15, 2011. Groundwater samples were collected using a peristaltic

173   pump with silicone tubing and were filtered (0.45 μm) in-line, prior to atmospheric

174   exposure. Samples for cation, NH_4^+ and PO_4^{3-} analyses were acidified to pH < 2

175   immediately after collection, whereas samples for anions, NO_3^- and artificial sweeteners

176   were left untreated. All samples were immediately transported to the laboratory where

177   they were either refrigerated at ~ 4° C or frozen (sweetener and NH_4 samples) until

178   analysis. Nitrate, Cl^- and SO_4^{2-} were analyzed in the Environmental Geochemistry

179   Laboratory (EGL), Department of Earth and Environmental Sciences, University of

180   Waterloo, ON, by ion chromatography using a Dionex ICS-90 (Dionex, Sunnyvale, CA),

181   which provided an analytical reporting limit of < 0.5 mg L^{-1} for each of these parameters.

182   NH_4^+ was also analyzed at EGL, using a colourimetric technique with a Beckman DU

183   530 spectrophotometer, which provided a detection limit of <0.05 mg L^{-1} N. PO_4^{3-} was

184   analyzed at the Soil and Nutrient Laboratory, University of Guelph, ON using a

185   colorimetric technique (cadmium reduction) with a Technicon TRAACS-800

186   autoanalyzer (Technicon Instruments, Tarrytown, NY), which provided a detection limit

187   of 0.05 mg L^{-1} P. Cations were analyzed at Canada Centre for Inland Waters (CCIW),

188   Burlington, ON, using an Inductively Coupled Plasma technique that provided detection

189   limits of 0.005-0.01 mg/L.   The four artificial sweeteners were also analyzed at CCIW,

190   by ion chromatography (Dionex 2500 system) coupled with tandem mass spectrometry

191   (AB Sciex QTRAP 5500 triple-quadrupole), following the methods described by Van

192   Stempvoort et al. (2011a). This technique provided a detection limit of 5 µg/L for

193   sucralose and much lower detection limits for sacharrin (0.021 µg/L), cyclamate (0.003

194   µg/L) and acesulfame (0.008 µg/L).

195

196   **^{3}H/^{3}He dating**

197   Seven new 5 cm diameter wells were also installed along the plume centreline in

198   2010, to facilitate trace gas sampling for ^{3}H/^{3}He age dating of the groundwater (Solomon

199   and Cook, 2000). These wells had short, 30 cm long, screened tips installed into the

200   plume core zone at locations immediately adjacent to wells 4 (4.4 and 6.4 m depth), well

201   7 (6.5 m), well 23 (6.5 m), well 14 (7.5 m), well 20 (6.5 m) and well 22 (6.4 m).

202   Sampling occurred by inserting diffusion-type samplers (Gardner and Solomon, 2009)

203   consisting of two 5 cm lengths of 4 mm dia. copper tubing connected with a 5 cm length

204   of 4 mm diameter, gas permeable silicone tubing. After purging the wells, the samplers

205   were inserted to the screen depths, for a period of one week during January 2011. Upon

206   removal from the wells, the copper tubes were immediately crimped and then shipped to

207   the Dissolved Gas Laboratory, University of Utah, Salt Lake City, UT, for analysis.

208   Noble gas analyses occurred by cryogenic separation followed by the measurement of

209   ^{3}He and ^{4}He on a MAP215-50 sector field mass spectrometer, and Ne, Ar, Kr, and Xe

210   measured on a quadrupole mass spectrometer operated in static mode. Coincident with

211   trace gas sampling, a 1L sample was retrieved from each well for analysis of tritium (^{3}H)

212   content. These were analyzed at the Environmental Isotope Laboratory, University of

213   Waterloo, after enrichment, which provided a reporting precision of $\pm$ 0.8-0.9 TU. Then

214   in February 2011, total dissolved gas pressures were measured in the seven trace gas

215   wells by inserting a downhole pressure probe (PT4 Tracker, Point Four Systems Inc.,

216   Coquitlam, BC, Canada) to the well screen depth and then slowing pumping the wells at

217   a rate that caused minimal drawdown (~0.5 L/min) until stable readings were obtained,

218   generally after about one hour. This is the procedure recommended by Roy and Ryan

219   (2010) to avoid measuring stagnant well bore water that may be partially degassed.

220

221   **Results and Discussion**

222   **Plume Ages**

223   As shown in Tables 3 and 4, dissolved Ne concentrations are all less than the

224   atmospheric equilibrium value, indicating that gas stripping has occurred. The ΔNe

225   values listed in Table 4 represent the percent deviation from atmospheric equilibrium and

226   range from -32% to -88%. The loss of noble gases appears to result from denitrification

227   that also produces total dissolved gas pressures that are significantly greater than the

228 atmospheric value (939 to 1046 mmHg for TDGP versus 756 for barometric pressure,

229 table 4). At shallow depths near the tile bed, the TDGP is only slightly less than the

230 confining pressure head (barometric pressure plus hydrostatic pressure), but this

231 difference increases at greater depths and greater distances from the tile drains (Table 4).

232 When the total dissolved gas pressure approaches or exceeds the confining pressure,

233 bubbles may form and result in stripping of sparingly soluble gases such as Ne and He

234 from the water. While it is clear from Table 4 that gas stripping is not occurring along

235 the axis of the plume (i.e. total dissolved gas pressures are always less than the confining

236 pressure), it is also apparent that at shallower depths near the water table beneath the tile

237 bed, gas stripping is likely. Furthermore, on a number of occasions it was observed that

238 some piezometer tubes (0.6 cm dia.) located near the tile bed would spontaneously erupt

239 without pumping. During these events an intermittent column of water and gas would

240 eject from the tubing for a period of about half a minute, thus degassing was actually

241 observed near the tile bed. These eruptions occurred only near the tile bed where

242 denitrification activity was most intense, and were not observed farther downgradient.

243 We have used these TDGP observations to formulate a model for calculating $^3H/^3He$ ages

244 that takes into account gas loss due to stripping. We followed the approach of Visser et

245 al. (2007), but included the occurrence of terrigenic ^4He, and we considered two end-

246 member cases of the stripping occurring either at the water table, or at the well (e.g.

247 stripping during sample collection). When stripping occurs near the water table

248 atmospheric He and Ne (that are used to separate tritiogenic from atmospheric ^3He

249 (Solomon and Cook, 2000)) are affected, but not the absolute amount of tritiogenic ^3He.

250 When stripping occurs at sampling, both atmospheric and tritiogenic ^3He are affected.

251   The general case where stripping occurs at some arbitrary point along a flow path

252   requires additional information or assumptions about where the stripping occurs (Visser

253   et al., 2007). Equations for calculating the apparent ^{3}H/^{3}He age under the conditions of

254   stripping at the water table and at the time of sampling are derived in Appendix A

255   (Supplemental Material). In addition to the loss of atmospheric gases, it is clear from

256   Table 4 that ^{4}He is being produced in the subsurface as it increases systematically with

257   distance along the plume. The age equations shown in Appendix A include a subsurface

258   source of ^{4}He known as terrigenic helium (Solomon and Cook, 2000) that results from

259   the decay of U and Th in the aquifer. While it is ^{3}He that is used for ^{3}H/^{3}He dating, the

260   production of ^{4}He should be accompanied by a small production of ^{3}He and this is taken

261   into account by specifying the ratio of ^{3}He/^{4}He of this source, known as $R_{terrigenic}$.

262   Figure 3 shows ^{3}H/^{3}He ages in the plume core zone computed assuming that

263   stripping occurs at the water table. Apparent age values are shown for two end-member

264   cases for $R_{terrigenic}$ of 2×10^{-8} and 4×10^{-7}. While an independent evaluation of $R_{terrigenic}$

265   is not available for this site, a value of 4×10^{-7} results in an age distribution that is

266   approximately 0 at the water table beneath the tile bed, and is more consistent with other

267   site data as explained below. In any case, the apparent ages range from 2 to 5 years in

268   well 24, 4.4 and 6.0 m depths, located 20 m from the edge of the tile bed, then increase

269   systematically along the plume to a maximum age of 13 to 17 years in well 22, 6.5 m

270   depth, located 200 m from the tile bed. The well 24 ages are corroborated by a previous

271   NaBr tracer test conducted in 2008 (Robertson et al., 2012), which showed that the plume

272   at well 124, 3 m depth, which is slightly closer (17 m from the edge of the tile bed), had a

273   slightly younger age of 0.8 years. The age indicated overall horizontal groundwater

274 velocity of the plume (200 m/15 yrs = 13 m/yr) is slightly slower, but is in general

275 agreement with, previous estimates of horizontal velocity in the shallower plume zone

276 closer to the tile bed (23 m/yr), based on seasonal breakthrough of an elevated EC spike

277 (Robertson, 2008). The approximate 15 year age estimate at the most distal location

278 (well 22) implies that the current monitoring network has sampled about three quarters of

279 the total plume length. Both the systematic increase in the ^{3}H/^{3}He ages and the TDGP

280 being less than the confining pressure, support a model of degassing occurring near the

281 water table. Alternatively, if it is assumed that degassing occurred in the well at the time

282 of sampling, unrealistically old ages of 30-40 years are obtained at several locations mid-

283 distance along the plume.

284

285 **Distribution of Indicator Parameters**

286 Figure 2 shows the distribution along the centreline, of three parameters (Cl$^-$, Na$^+$

287 and EC) that are often elevated in contaminant plumes and that have been used

288 previously as indicator parameters. Figure 4 profiles the concentrations of these

289 constituents along the plume core zone and in the upgradient wells, and compares these

290 to mean values measured in the septic tank effluent (Table 1). EC remains elevated

291 throughout the plume core zone (903-1616 μS/cm) which contrasts with lower values in

292 the up-gradient wells (379-500 μS/cm) by a factor of 2-4. Cl$^-$ is more distinctly elevated

293 in the plume (31-99 mg/L), which is 3-150 times higher than in the upgradient wells (0.6-

294 13 mg/L). However in the down gradient area, some of the groundwater overlying the

295 plume has very high Cl$^-$ of up to 112 mg/L, which is higher than in the plume. This is

296 likely a result of the use of the dust suppressant $CaCl_2$ on the campground roadways. Na$^+$,

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297   on the other hand is consistently elevated throughout the plume (11-49 mg/L) at

298   concentrations that are generally >100 times higher than values occurring in both in the

299   upgradient wells and in the $CaCl_2$ impacted wells.

300

301   **Distribution of Nutrients and Pathogens**

302   Figure 5 shows the distribution of three nutrients that are normally elevated in

303   domestic wastewater (NH_4^+-N, NO_3^--N and PO_4^{3-}-P) and E. coli. bacteria, along the

304   plume centreline. Figure 6 profiles the concentrations of the nutrients along the core

305   zone. The nutrients are elevated in the septic tank effluent (8-100 mg/L, Table 1) and

306   occur intermittently at similarly high concentrations in the shallow groundwater below

307   the tile bed (NH_4^+-N up to 20 mg/L; NO_3^--N up to 103 mg/L and PO_4^{3-}-P up to 6.8 mg/L).

308   However, beyond 50 m from the tile bed, all of these constituents decline to non-

309   detectable levels, indicating that significant attenuation has occurred. This is consistent

310   with previous studies at this site which showed that; NO_3^- is depleted by denitrification,

311   utilizing trace quantities of organic carbon and pyrite present in the aquifer sediments

312   (Aravena and Robertson, 1998), that NO_3^- and NH_4^+ are also attenuated by anaerobic

313   ammonium oxidation (anammox, Robertson et al., 2012) and that PO_4^{3-} migration

314   velocity is retarded by a factor of about 25 by adsorption (Robertson, 2008). These

315   constituents are thus less useful as indicator parameters at this site because of these

316   vigorous attenuation processes. The low level NH_4^+-N that occurs in the distal plume

317   zone (1-3 mg/L, Fig. 5) has an isotopic signature that is distinctly lighter ($^{15}N = +4.3 \pm$

318   1.2 per mil, n=5, EGL internal data) compared to the wastewater NH_4^+-N that occurs

319   immediately downgradient of the tile bed ($^{15}N = +19 \pm 6.4$ per mil, n= 25, Robertson et

320   al., 2012) and is therefore not likely of wastewater origin. This could represent natural

321   NH_4^+ mineralized from organic rich zones that may be present near the base of the

322   aquifer or in the underlying silt unit.

323

324   **Distribution of other Major Ions**

325   Figure 7 shows the distribution of several other major ions (K^+, Ca^{2+}, SO_4^{2-}-S)

326   along the plume centreline, while Fig. 4 profiles the concentrations of K^+ and Ca^{2+} along

327   the core zone. K^+ is elevated in the proximal plume zone (6-47 mg/L) by a variable

328   factor of about 1-400 compared to the upgradient wells, however in the distal plume zone

329   K^+ concentrations (2-5 mg/L) are virtually the same as in the overlying background

330   groundwater. Elevated K^+ values in the proximal plume (>5 mg/L) decline abruptly

331   beyond 115 m from the tile bed, which may be suggestive of a sorption front with

332   indicated retardation factor of about 2-3. This is consistent with K^+ retardation factors

333   observed in other contaminant plumes in sand aquifers (2-4, Nicholson et al., 1983;

334   Ceazan et al., 1989). Ca^{2+} in the plume (120-269 mg/L) is elevated by a factor of 2-4

335   compared to both the upgradient wells and the septic tank effluent. Presumably this is a

336   result of calcite dissolution that occurs in response to acidity generated by the wastewater

337   oxidation reactions occurring in the vadose zone, particularly NH_4^+ oxidation. SO_4^{2-}-S is

338   sporaticly elevated in the plume, with highest values (up to 50 mg/L) occurring in the

339   basal zone where NO_3^- becomes depleted. Presumably this reflects denitrification

340   utilizing pyrite from the aquifer sediments as the electron donor (Aravena and Robertson,

341   1998).

342

343   **Distribution of Artificial Sweeteners**

344   Figure 8 shows the distribution of the four artificial sweeteners (acesulfame,

345   cyclamate, sucralose, saccharin) along the plume centreline, while Fig. 9 profiles the

346   concentrations of these constituents along the plume core zone. All four sweeteners occur

347   in the septic tank effluent at similar mean concentrations (15-51 µg/L, Table 1).

348   However, whereas acesulfame and sucralose persist in the proximal plume at

349   concentrations that are similar to the septic tank effluent, cyclamate and sacharrin occur

350   at much lower concentrations in the plume (<10 % of tank values), indicating that they

351   are likely influenced by degradation reactions in the vadose zone. Although sucralose is

352   elevated throughout the proximal plume zone (15-77 µg/L), it has a much higher

353   analytical detection limit (5 µg/L) compared to the other compounds (0.003-0.02 µg/L)

354   and is thus only elevated by a factor of 3-15 compared to background values. Also

355   sucralose values decline abruptly to background levels beyond 60 m from the tile bed.

356   This could reflect a sorption front or it could indicate increasing consumer use of this

357   sweetener in recent years. Acesulfame on the other hand, because of its much lower

358   detection limit, is elevated by a much larger factor (>1000) compared to background

359   values even in the distal plume zone 200 m from the tile bed (8-18 µg/L). There is no

360   evidence of abrupt acesulfame depletion anywhere along the plume. Although cyclamate

361   is considerably attenuated in the plume compared to the effluent, it does persist

362   throughout the distal plume zone at concentrations of 1-2 µg/L, which still represents

363   enrichment by a factor of ~ 500 compared to background detection limit values.

364   .

365   **Persistance of EC, Cl, Na, and Acesulfame**

366   Figure 10 shows normalized concentration profiles (C/C_o) of four constituents

367 (EC, Cl^-, Na^+ and acesulfame) that appear relatively mobile and persistent along the full

368 length of the plume. Comparing normalized values could provide insight into processes

369 that may be affecting these constituents differently. Initial concentrations (C_o) were

370 calculated as the mean values measured in the four multilevel bundles underlying the tile

371 bed (wells 120-123), because these provide a larger data set (n = 20) that probably better

372 reflects effluent composition and loading under all seasonal conditions. With the

373 exception of Cl^-, which begins to increase beyond 150 m from the tile bed, all of these

374 parameters show similar slow declining trends along the plume without abrupt changes.

375 In the distal plume zone (wells 21 and 22), the mean EC value (926 µS/cm, n = 4) is 74%

376 of the mean value below the tile bed, Na^+ (14.7 mg/L) is 43%, acesulfame (12.1 µg/L) is

377 23% and Cl^- (71.5 mg/L) is 137%. EC and Cl^- appear to be affected by dispersive

378 dilution with overlying background groundwater that has lower EC but which has locally

379 higher Cl^- as result of the use of $CaCl_2$ on the campground roadways. Na, in addition to

380 advective dilution, could be depleted by weak adsorption. Acesulfame, in addition to the

381 above processes could be influenced by increasing consumer use in recent years,

382 although we are not aware of any records that document usage trends in Canada. Also,

383 the introduction of water limiting fixtures in the washroom in ~2004, which has increased

384 the effluent strength in recent years (Table 2), also likely contributes to the higher values

385 observed near the tile bed. Nonetheless, all of these parameters (with the possible

386 exception of Cl^-), remain indicative of the wastewater source throughout the full length of

387 the plume. Furthermore, during campground start up in May 2011, all of these parameters

388 (Cl^-, Na^+ and acesulfame), arrived at the water table below the tile bed simultaneously

389   (Fig. 11), indicating that none of these are strongly affected by sorption in the vadose

390   zone sediments. Saccharin and cyclamate also arrived at the water table at the same time

391   (Fig. 11), indicating a similar lack of sorption effect. However, the water table values for

392   saccharin and cyclamate then both slowly declined to < 1 µg/L by July 2011. The septic

393   tank values for acesulfame (43 $\pm$ 8 µg/L, n=8, May 24-July 8, 2011), saccharin (12.4 $\pm$

394   2.9 µg/L, n = 8) and cyclamate (36.5 $\pm$ 38.7, n = 8) all remained consistently high

395   throughout this period (> 8 µg/L). This behaviour indicates that both saccharin and

396   cyclamate are affected by degradation in the vadose zone (aerobic), although a seasonal

397   acclimation period of several weeks duration is apparently required. Sucralose was not

398   detected (<5 µg/L) in the septic tank effluent during the period May 24-June 15 (n = 5),

399   for reasons that were not apparent, but then concentrations increased thereafter. Sucralose

400   values at the water table (Fig. 11) closely mirrored septic tank values throughout this

401   period.

402   Comparison of the normalized plots of EC, Na^+, Cl^- and acesulfame along the

403   plume (Fig. 10) suggests that over time, input concentrations of acesulfame in the

404   wastewater may have increased at Long Point. Assuming that attenuation of acesulfame

405   in the plume has been similar to that of the other indicators, particularly Na (i.e.,

406   negligible biodegradation), then on the basis of the observed trends in normalized

407   concentrations at the various points along the plume, with inferred ages ranging from

408   about 2-15 years, it appears that acesulfame concentrations may have increased steadily

409   over the past 15 years, and that they may have doubled since ~1995 (the approximate age

410   of the oldest part of the plume that was investigated). Given that there are no studies that

411   have documented changes in acesulfame concentrations in 'domestic' wastewater in

18

412   Canada since its approval for use in 1988, this plume data is apparently the best available

413   proxy / surrogate record of inferred changes in acesulfame concentrations in domestic

414   wastewater in Canada. Even if the acesulfame trend is partly the result of slow

415   biodegradation, the degradation rate must be exceedingly slow (half life > 15 years) and

416   the acesulfame concentrations in the 1995 wastewater must have been at least 50% of

417   current values.

418

419   **Implications**

420   Na^+ is monovalent cation that is affected by adsorption, but only weakly so, and

421   in most aquifers its migration velocity is close to that of Cl^- (Nicholson et al.,1983; Dance

422   and Reardon, 1983; Robertson et al.,1991). The simultaneous breakthrough of elevated

423   Cl^- and Na^+ at the water table during spring 2011 startup, (Fig. 11), is consistent with a

424   minimal sorption effect. Thus, Na^+ can be considered a mobile tracer in many aquifer

425   environments. Furthermore, the Na^+ contrast with background groundwater at this site

426   remains large (> 100), even in the downgradient area where there could be some

427   anthropogenic influence from the campground. Na^+ was used previously as the preferred

428   intrinsic tracer for identifying a septic system plume in agricultural terrain in southern

429   Ontario (Cambridge site, Robertson et al., 1991) because Na^+ remained low in the

430   background groundwater (mean of 4 mg/L) compared to much higher values in the septic

431   system plume (mean of 86 mg/L). However, in a larger scale (12 km^2) regional survey of

432   shallow (<30 m) overburden wells (n = 29), in other agricultural terrain near the city of

433   Woodstock, also in southern Ontario, considerably higher Na^+ values, mostly in the range

434   of 5-25 mg/L, were observed (Heagle, 2000). Higher Na^+ values in the Woodstock area,

435   likely reflected additional input from road salt and manure applications, making Na^+ less

436   useful as a wastewater tracer in such areas.

437   The persistence of acesulfame throughout the plume at concentrations more than

438   1000 times higher than background detection-limit values, points to the considerable

439   potential of this trace organic constituent as an intrinsic wastewater tracer. Such high

440   enrichment offers the potential to allow detection of even very small inputs from

441   wastewater. Acesulfame was also detected previously in 65 of 100 monitoring wells

442   sampled near Zurich Switzerland (Buerge et al., 2009) and in more than 60% of ~300

443   samples collected in a broad-based screening survey in Canada (Van Stempvoort et al.,

444   2011a), which included samples from groundwater wells in Ontario and the Yukon,

445   groundwater along streams in Alberta, and surface water from five streams effected by

446   urban development in Ontario and Alberta. Acesulfame concentrations should be further

447   screened in other septic system plumes and in other groundwater environments. These

448   should include agriculturally impacted sites because sweeteners can be included in

449   animal feed formulations in some jurisdictions (Buerge et al., 2011) and could thus be

450   present where groundwater is impacted by manure applications. If, however, acesulfame

451   is shown to be uniquely enriched in domestic wastewater and remains mobile and

452   persistent in other aquifer environments, then in cases of groundwater NO_3^-

453   contamination for example, the ratio of NO_3^-/acesulfame might be developed as a new

454   tool for establishing the faction of NO_3^- loading originating from agricultural versus

455   domestic wastewater sources.

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559 Table 1. Mean composition of the Long Point septic tank effluent in recent studies (2007-
560 2011).

561

	Mean $\pm$ s.d.	n
Major ions [1] (mg/L)		
Cl^- [1,2]	83 ± 31	20
Na^+	36 ± 9	10
Ca^{2+}	137 ± 31	9
SO_4^{2-}-S	6.6	1
K^+	25 ± 8	10
Nutrients (mg/L)		
NH_4^+-N [1,2]	100 ± 27	23
NO_3^-- N [2]	<2	11
Sweeeteners [1,3] (μg/L)		
Acesulfame	50 ± 15	13
Sucralose	51 ± 42	13
Cyclamate	29 ± 37	13
Saccharin	15 ± 5	13

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563 1) May 19-July 8, 2011, this study

564 2) Sept 18, 2007-June 8, 2010, Robertson et al. (2012)

565 3) June, 2008- Oct 4, 2010, Van Stempvoort et al. (2011b)

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571 Table 2. History of wastewater composition in the Long Point septic tank effluent over
572 20 years of operation. Shown are mean values over 1-3 year periods (n, number of
573 samples).

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Year	n	EC (µS/cm)	Cl⁻ (mg/L)	Na⁺ (mg/L)	NH_4^+-N (mg/L)	PO_4^{3-}-P (mg/L)	reference
1989-1990	6		44	35	66	6	Robertson and Cherry (1992)
1995	1		42	23	57	11.8	Robertson et al.(1998)
2004	2	1243	74	47	88	7.5	Carrara (2006); Robertson (2008)
2007-2010	10-13		67		106		Robertson et al. (2012)
2011	9-10	1662	97	36	92		This study

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578   Table 3. Noble gas and tritium concentrations.

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Well	Distance from source (m)	Ar (ccSTP/g)	Ne (ccSTP/g)	Kr (ccSTP/g)	Xe (ccSTP/g)	He (ccSTP/g)	R/Ra	Tritium (TU)
LP24-4.4	20	3.09E-04	1.29E-07	7.61E-08	1.03E-08	3.45E-08	0.874	10.0
LP24-6.0	23	2.53E-04	1.12E-07	6.59E-08	9.89E-09	3.69E-08	0.741	9.9
LP7-6.4	60	2.86E-04	1.34E-07	8.03E-08	1.13E-08	3.93E-08	0.896	10.7
LP13-6.5	95	1.37E-04	2.57E-08	4.22E-08	7.05E-09	4.33E-08	0.543	10.0
LP23-6.4	108	1.46E-04	3.72E-08	4.29E-08	7.44E-09	5.11E-08	0.502	9.2
LP20-7.3	160	1.77E-04	4.80E-08	5.09E-08	8.18E-09	4.73E-08	0.734	9.7
LP22-6.3	200	2.74E-04	1.13E-07	7.50E-08	1.12E-08	5.39E-08	0.878	9.1

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583 Table 4. ΔNe, apparent ages with end-members values for R_{terr}, terrigenic ^{4}He, and
584 TDGP. Confining pressure (CP) is hydrostatic pressure at the well screen depth plus
585 atmospheric pressure of 756 mmHg.

586

Well	delta Ne %	Apparent Age (yr) with Rterr = 2e-8	Apparent Age (yr) with Rterr = 4e-7	Age error (yr)	4Heterr (ccSTP/g)	TDGP (mmHg)	CP (mmHg)
LP24-4.4	-33.5	4.8	2.7	0.4	9.4E-09	939	952
LP24-6.0	-41.7	5.4	1.9	0.4	1.6E-08	1029	1063
LP7-6.4	-32.2	6.7	4.3	0.4	1.2E-08	1032	1103
LP13-6.5	-88.4	12.7	6.5	0.5	3.9E-08	1046	1088
LP23-6.4	-82.6	13.5	5.8	0.5	4.5E-08	999	1040
LP20-7.3	-77.3	16.3	11.2	0.5	3.9E-08	988	1020
LP22-6.3	-43.7	16.9	12.7	0.6	3.2E-08	950	1016

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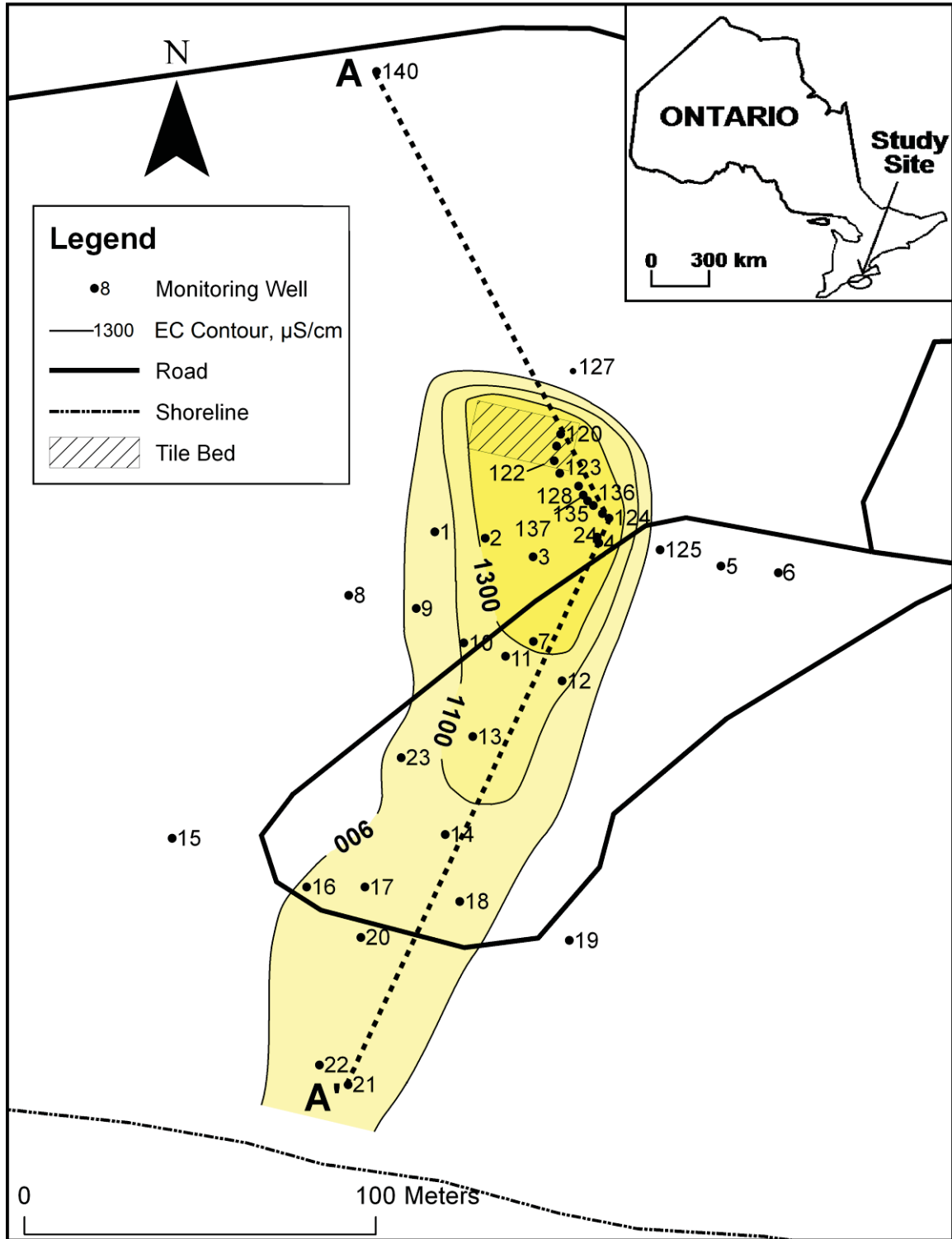
Fig. 1. Long Point septic system site showing location of the tile bed, multilevel monitoring wells and contours of maximum electrical conductivity (EC) measured in the monitoring wells October, 2010.

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600   Fig. 2. Distribution of indicator parameters along the plume centreline, October, 2010: a)
601   Cl⁻, b) Na⁺ and C) electrical conductivity (EC). Dashed line indicates plume core zone
602   indicated by Na⁺ > 10 mg/L. Note changes in distance scale.
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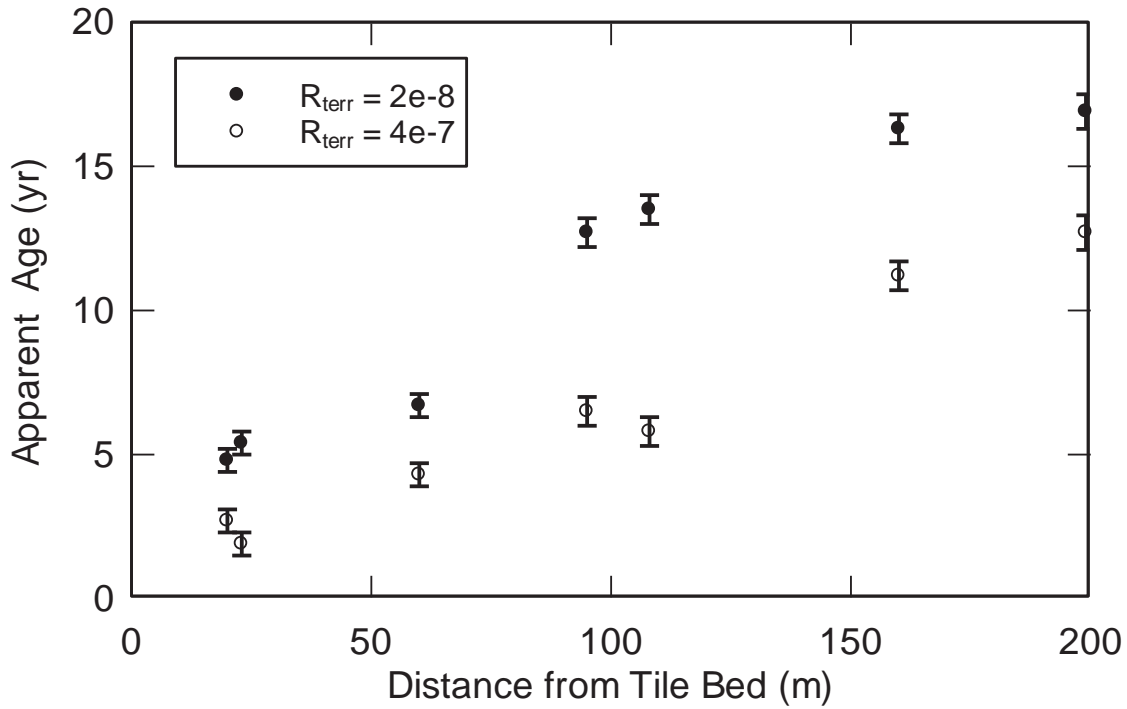
Fig. 3. Groundwater age profiles along the plume core zone determined by ^{3}H/^{3}He dating. Ages assume degassing occurred near the tile bed area. Ages were computed using two end-member values for ratio of ^{3}H/^{4}He for terrigenic He production (R_{terr}). The ages computed using $R_{terr} = 4 \times 10^{-7}$ are more consistent with the site data (see text).

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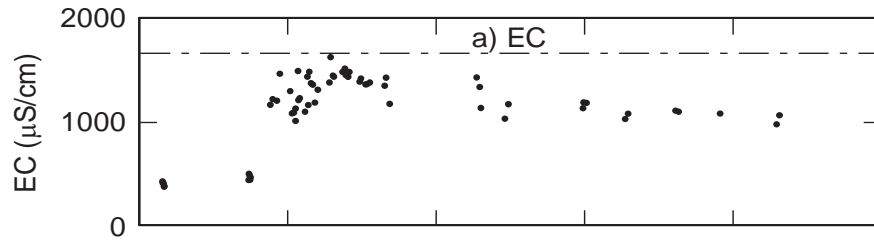
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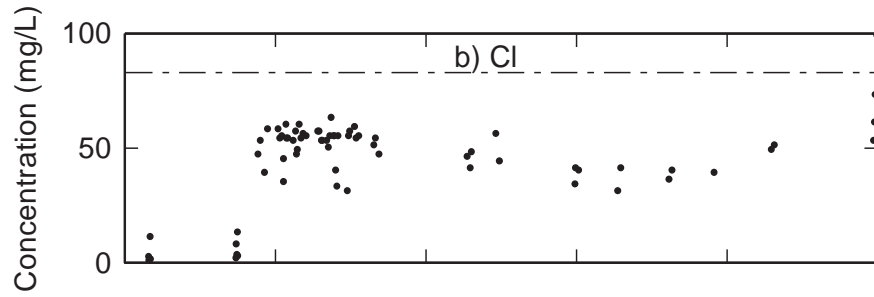
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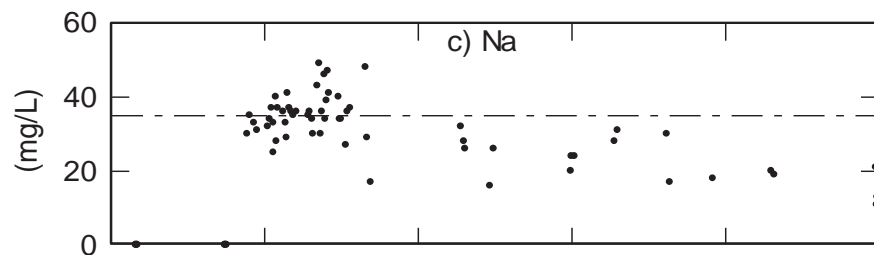
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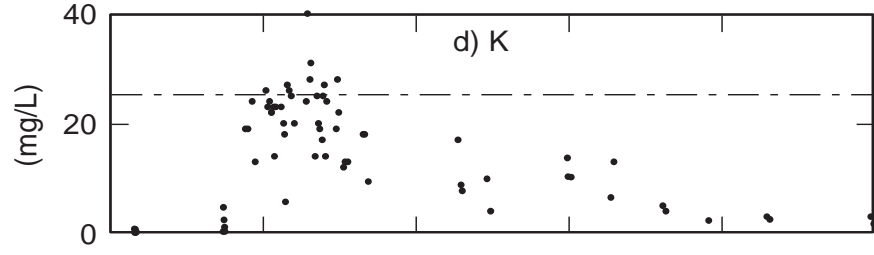
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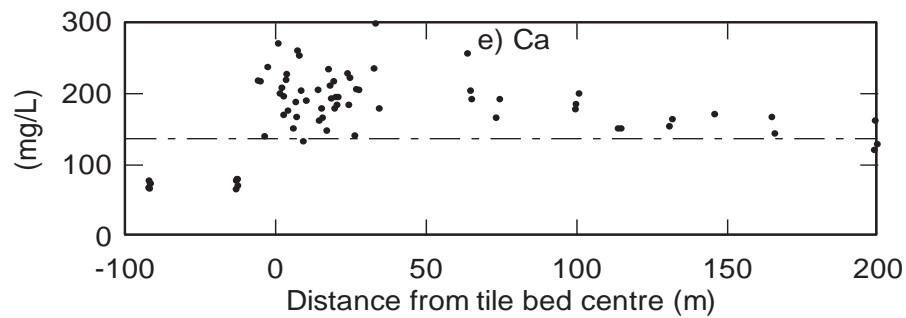
619   Fig. 4. Concentration profiles of major ions along the plume core and in upgradient
620   wells: a) electrical conductivity (EC), b) Cl^-, c) Na^+, d) K^+ and e) Ca^{2+}. Dashed line is
621   mean septic tank value from Table 1. Core zone wells defined by $Na^+ > 10$ mg/L. Note
622   change of distance scale upgradient of the tile bed.
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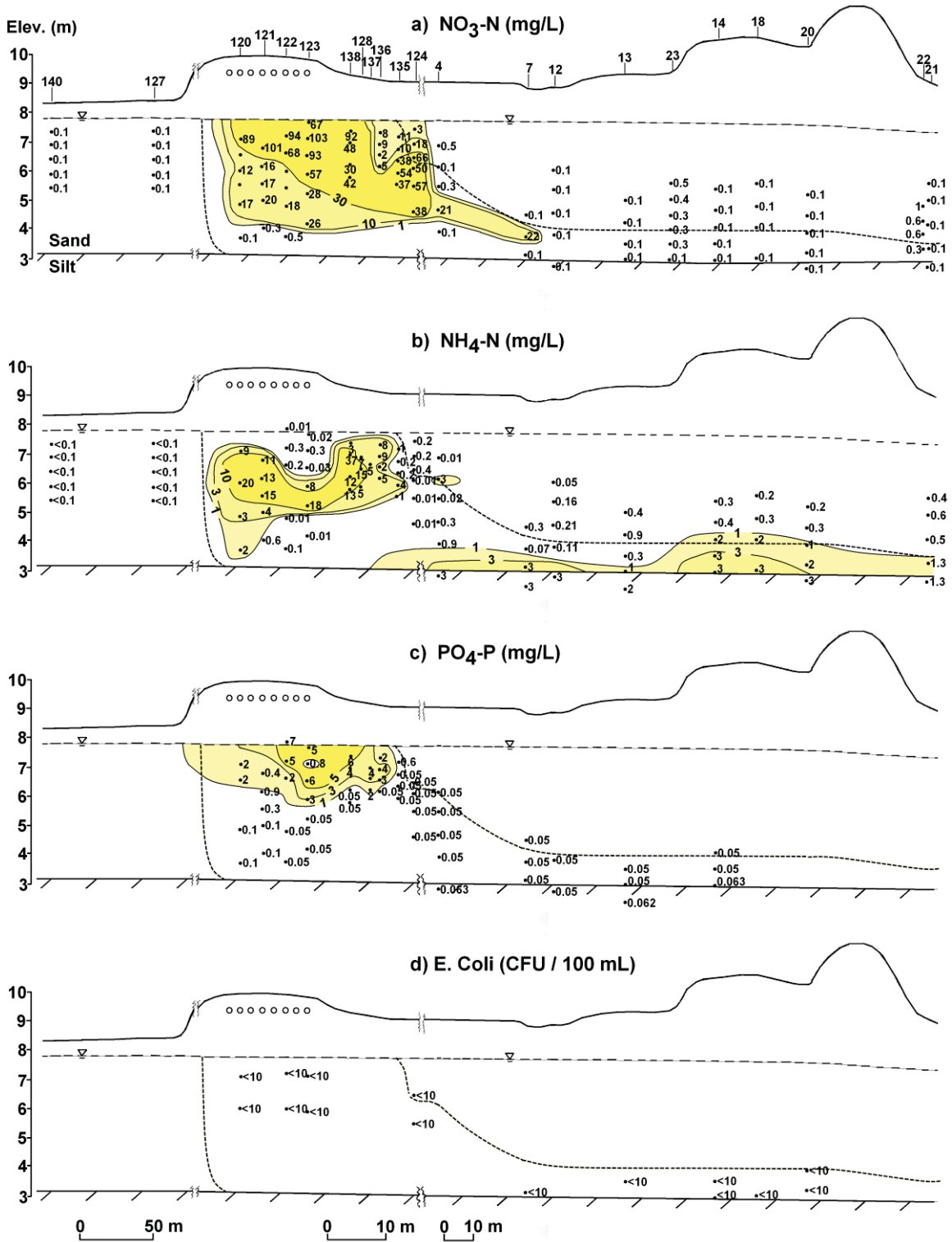
Fig. 5. Distribution of nutrients and pathogens along the plume centreline October, 2010:
a) NO_3^--N, b) NH_4^+-N, c) $PO_4^{3-}-P$ and d) E. coli. Dashed line indicates plume core zone
($Na^+ > 10$ mg/L).

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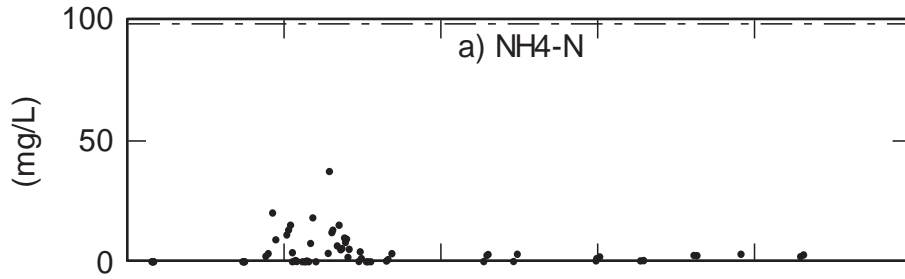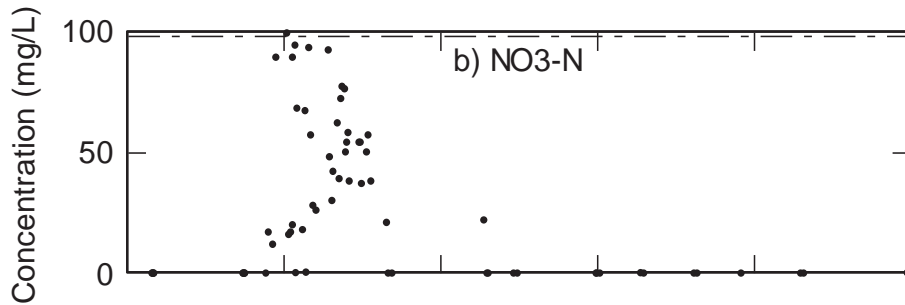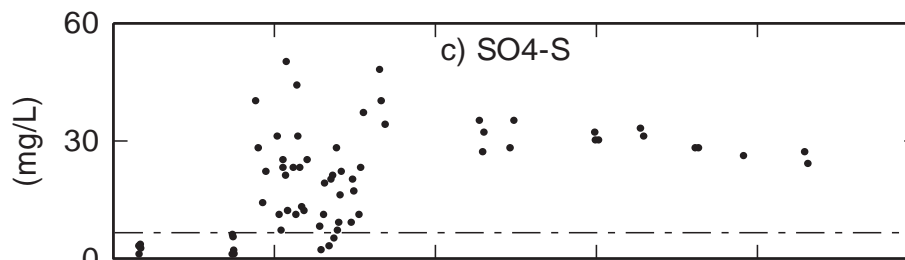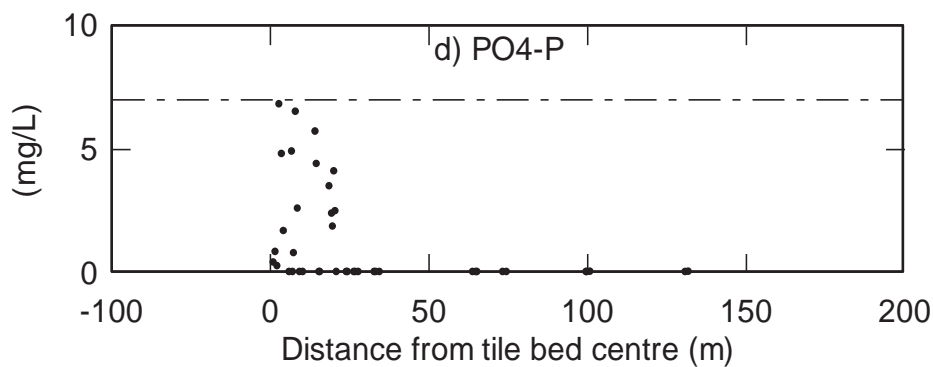
Fig. 6. Concentration profiles of nutrients and SO_4^{2-}-S along the plume core and in upgradient wells: a) NH_4^+-N), b) NO_3^--N, c) SO_4^{2-}- S and d) PO_4^{3-}- P. Note that NH_4^+-N septic tank mean value from Table 1 (dashed line) is used for both NH_4^+ and NO_3^- panels.

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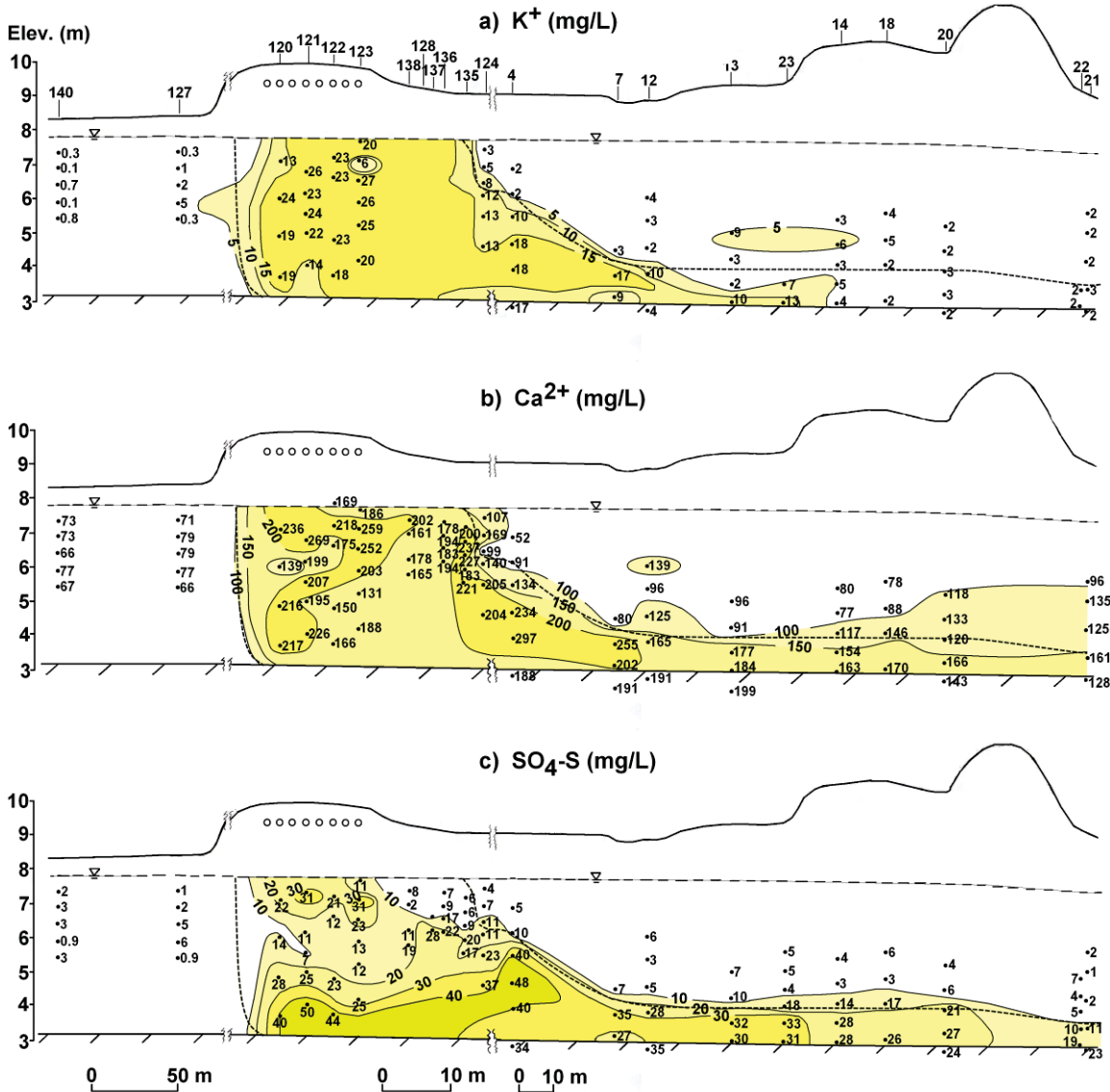
Fig. 7. Distribution of other major ions along the plume centreline, October, 2010: a) K^+, b) Ca^{2+}, and c) SO_4^{2-}-S. Dashed line indicates plume core zone ($Na^+ > 10$ mg/L).

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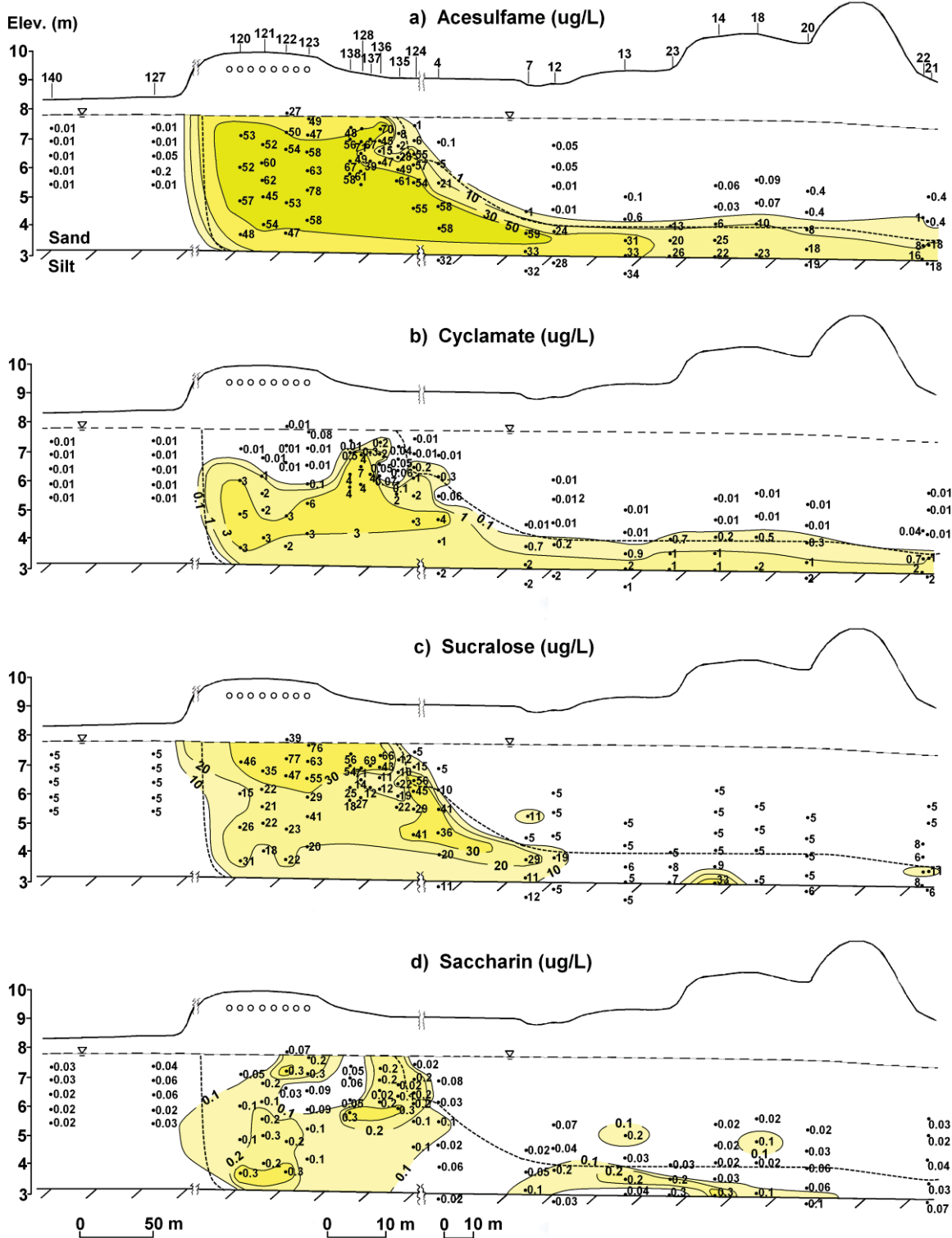
Fig. 8. Distribution of four artificial sweeteners along the plume centre line, October, 2010: a) acesulfame, b) cyclamate, c) sucralose and d) sacharrin. Dashed line indicates plume core zone ($Na^+ > 10$ mg/L).

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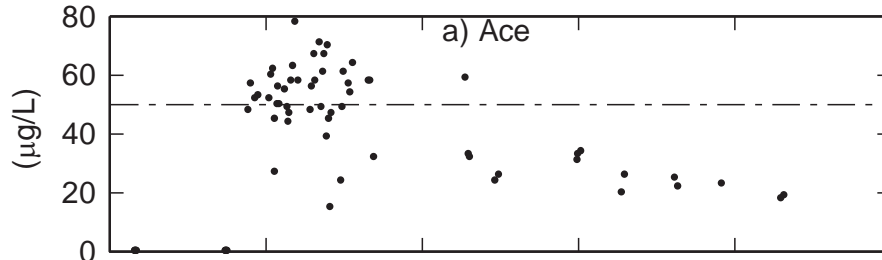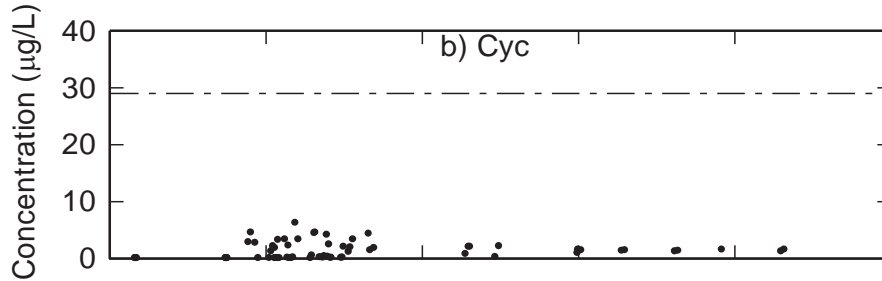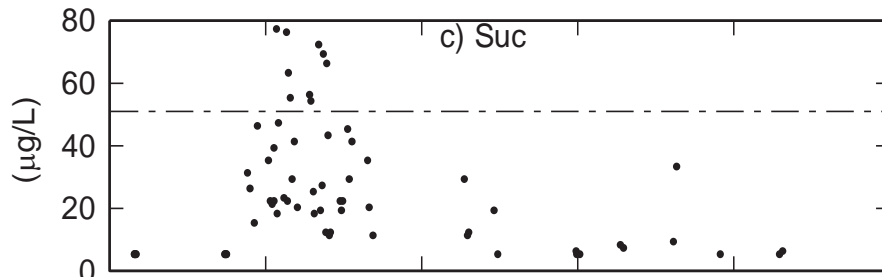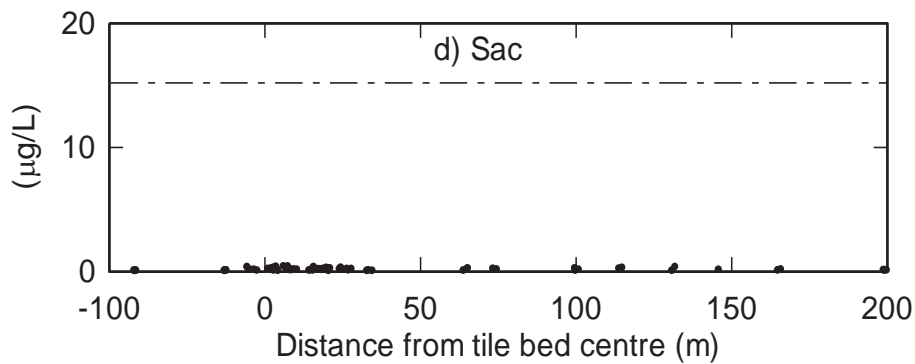
Fig. 9. Concentration profiles of artificial sweeteners along the plume core and in upgradient wells: a) acesulfame, b) cyclamate, c) sucralose and d) sacharrin. Dashed lines are mean septic tank values from Table 1.
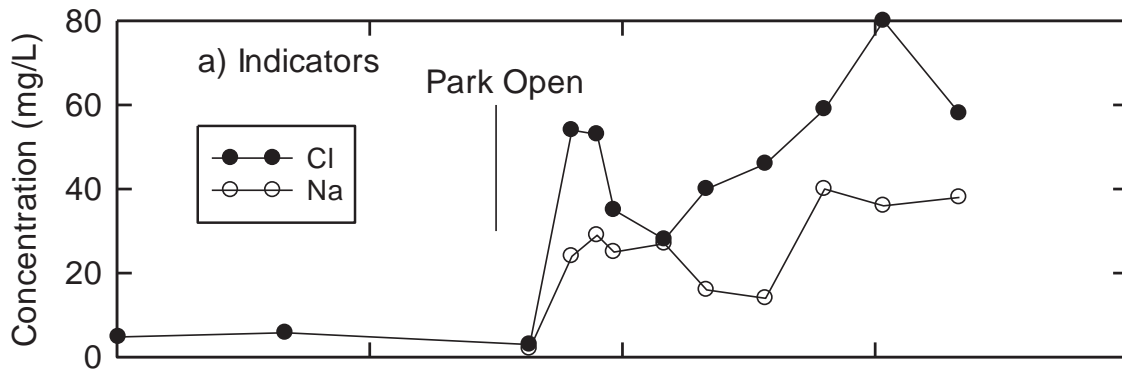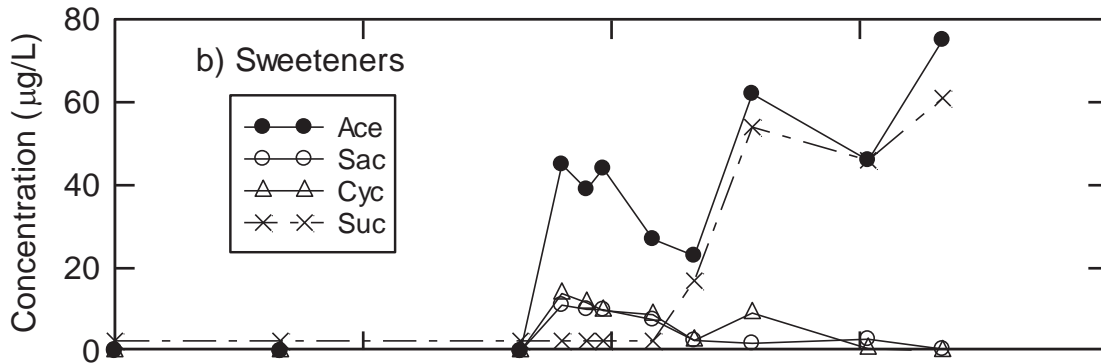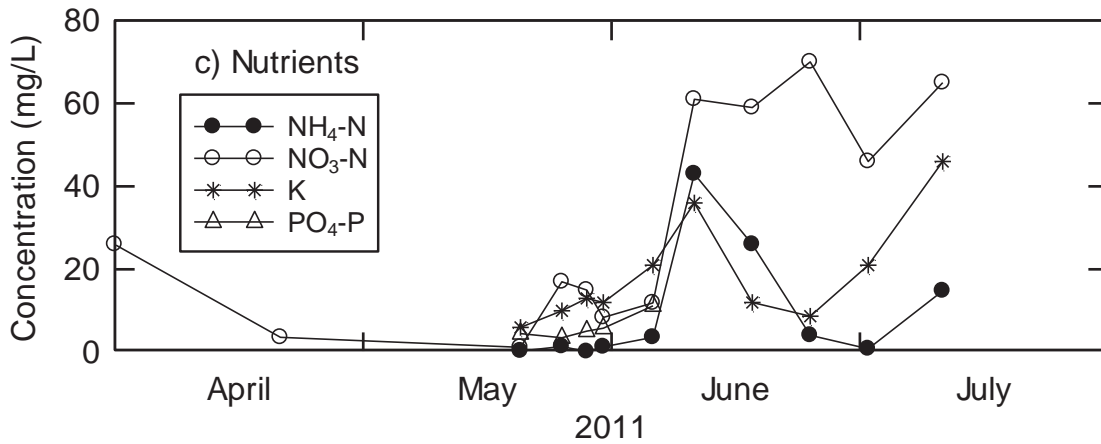
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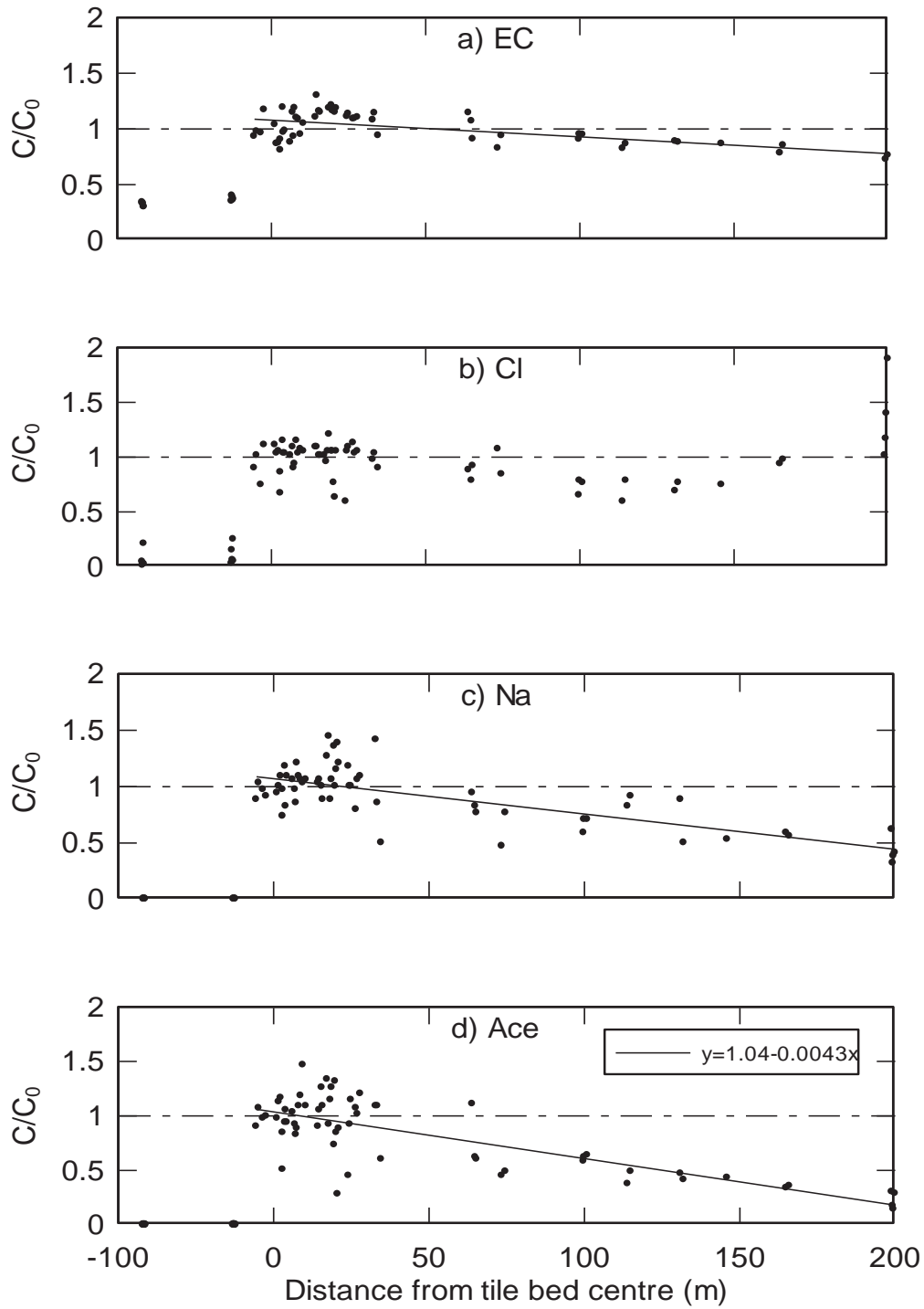
Fig. 10. Normalized concentrations (C/C_0) of indicator parameters along the plume core zone: a) EC, b) Cl^-, c) Na^+, and d) acesulfame. C_0 values are mean values under the tile bed in bundles 120-123, n = 20 (EC, 1244 µS/cm; Cl^-, 52.2 mg/L; Na^+, 33.9 mg/L; acesulfame, 53.2 µg/L).

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Fig. 11. Breakthrough of wastewater constituents in the shallow water table zone below the tile bed (well 122-2.2 m depth) during campground start-up, spring, 2011: a) indicator parameters, b) artificial sweeteners and c) nutrients. Abrupt increases occurred on May 24, 2011, the day after the first heavy use weekend.

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682 **Appendix A (Supplemental Material)**

683 **Evaluation of tritium/helium-3 ages when degassing has occurred.**

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685 We have followed the approach of Visser et al. (2007), but include terrigenic ^{4}He and

686 consider the two end member cases of (1) degassing at the water table, and (2) degassing

687 at the time of sampling.

688

689 Case #1 Degasing at the water table with no original excess air.

690

691 The ^{3}He balance in a sample is:

692 $^3He_s = {}^3He_{eq} f_{{}^3He} + {}^3He_s^* + {}^3He_{terr}$ (Eq. 1)

693 where the subscripts stand for s = sample, eq = equilibrium (sometimes referred to as

694 solubility) terr = terrigenic and

695 $f_{{}^3He} = \dfrac{1}{1 + H_{He}\square V_g}$ is the fraction of ^{3}He in solution after degassing has occurred, and

696 $V_g = \dfrac{\dfrac{1}{\square Ne + 1} \square 1}{H_{Ne}}$ isthe gas phase volume,

697 $\square Ne = (\dfrac{Ne_s}{Ne_{eq}} \square 1)$ is the neon deviation from atmospheric solubility,

698 H_{He} is the dimensionless Henrys coefficient for helium, and

699 H_{Ne} is the dimensionless Henrys coefficient for neon.

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701

702 The superscript * stands fortritiogenic (i.e. derived from tritium decay). For each of the

703 subscripted quantities, we define the ratio of ^{3}He to ^{4}He (e.g. $R_s = \dfrac{{}^3He_s}{{}^4He_s}$)

704 and substitute these ratios into Eq. 1 to obtain

705

706 $^3He_s^* = {}^4He_s R_s \square f_{{}^3He} {}^4He_{eq} R_{eq} \square {}^4He_{terr} R_{terr}$ (Eq. 2)

707 The ^{4}He balance leads to the following expression for terrigenic ^{4}He

708 $^4He_{terr} = {}^4He_s \square {}^4He_{eq} f_{{}^3He}$ (Eq. 3)

709 Substituting Eqs. 2 and 3 into the equation of radioactive decay for tritium leads to

710 $t = \dfrac{Ln\square\dfrac{{}^3He_s^*}{{}^3H_s} + 1\square}{\square}$ (Eq. 4)

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712 Case #2 Degasing at the time of sample collection with no original excess air

713 The ^{3}He balance is

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714    $^{3}He_{s} = \left(^{3}He_{eq} + {}^{3}He^{*} + {}^{3}He_{terr} \right) f_{^{3}He} = f_{^{3}He} {}^{3}He_{eq} + {}^{3}He_{s}^{*} + {}^{3}He_{terrs}$ (Eq. 5)

715   Substituting the ^{3}He/^{4}He ratios as defined above and solving for $^{3}He_{s}^{*}$ we have

716    $^{3}He_{s}^{*} = {}^{4}He_{s}R_{s} \square f_{^{3}He} {}^{4}He_{eq}R_{eq} \square {}^{4}He_{terrs}R_{terr}$ (Eq. 6)

717   The ^{4}He balance leads to the following expression for terrigenic^{4}He

718    $^{4}He_{terrs} = {}^{4}He_{s} \square {}^{4}He_{eq}f_{^{3}He}$ (Eq. 7)

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720   Substituting Eqs. 6 and 7 into the equation of radioactive decay for tritium leads to

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722    $t = \dfrac{Ln\left[\dfrac{^{3}He_{s}^{*}}{f_{^{3}He} {}^{3}H_{s}} + 1 \right]}{\square}$ (Eq. 8)

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