Water Research 88 (2016) 653–660

Contents lists available at ScienceDirect

Water Research

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

# Degradation of sucralose in groundwater and implications for age dating contaminated groundwater

W.D. Robertson [a, *], D.R. Van Stempvoort [b], J. Spoelstra [a, b], S.J. Brown [b], S.L. Schiff [a]

[a] University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada
[b] Environment Canada, Burlington, Ontario, Canada

ARTICLE INFO

*Article history:*
Received 12 June 2015
Received in revised form
24 October 2015
Accepted 26 October 2015
Available online 11 November 2015

*Keywords:*
Wastewater
Tracers
Groundwater
Sweeteners

ABSTRACT

The artificial sweetener sucralose has been in use in Canada and the US since about 2000 and in the EU since 2003, and is now ubiquitous in sanitary wastewater in many parts of the world. It persists during sewage treatment and in surface water environments and as such, has been suggested as a powerful tracer of wastewater. In this study, longer-term persistence of sucralose was examined in groundwater by undertaking a series of three sampling snapshots of a well constrained wastewater plume in Canada (Long Point septic system) over a 6-year period from 2008 to 2014. A shrinking sucralose plume in 2014, compared to earlier sampling, during this period when sucralose use was likely increasing, provides clear evidence of degradation. However, depletion of sucralose from a mean of 40 μg/L in the proximal plume zone, occurred at a relatively slow rate over a period of several months to several years. Furthermore, examination of septic tank effluent and impacted groundwater at six other sites in Canada, revealed that sucralose was present in all samples of septic tank effluent (6–98 μg/L, n = 32) and in all groundwater samples (0.7–77 μg/L, n = 64). Even though sucralose degradation is noted in the Long Point plume, its ubiquitous presence in the groundwater plumes at all seven sites implies a relatively slow rate of decay in many groundwater septic plume environments. Thus, sucralose has the potential to be used as an indicator of 'recent' wastewater contamination. The presence of sucralose identifies groundwater that was recharged after 2000 in Canada and the US and after 2003 in the EU and many Asian countries.



## 1. Introduction

Some trace organic constituents that are unique to sanitary wastewater, persist during sewage treatment and in aqueous environments and consequently, several are being used as tracers to fingerprint the presence of sanitary wastewater in surface water and groundwater environments. These tracers include the pharmaceutical compound carbamazepine (e.g. Clara et al., 2004; Van Stempvoort et al., 2013) and the artificial sweetener potassium acesulfame (e.g. Buerge et al., 2009; Spoelstra et al., 2013), widely used in diet soft drinks and other food products. These two compounds have garnered attention because they occur in sanitary wastewater at concentrations that are orders of magnitude above background levels and thus, they offer the potential to reveal the presence of even very small amounts of wastewater. For example, in a screening survey of 100 wells in Switzerland, acesulfame (ACE) was detected in 65 of the samples (Buerge et al., 2009) and in a study of a urban groundwater in Canada, ACE was detected in >50% of the samples from seven different sites (Van Stempvoort et al., 2011a). Wolf et al. (2012) measured a suite of 71 trace organic constituents in a network of monitoring wells testing for sewer leakage in the city of Rastatt, Germany and detected carbamazepine and ACE most frequently, (33 and 28% of samples respectively).

Another commonly used artificial sweetener, sucralose (SUC), has also become ubiquitous in sanitary wastewater in many parts of the world. It too exhibits minimal removal during sewage treatment (Buerge et al., 2009; Schmid Neset et al., 2010; Lange et al., 2012; Tran et al., 2014; Subedi and Kannan, 2014) and during the production of potable water supplies (Mawhinney et al., 2011) and consequently, has also been proposed as a tracer for detecting sanitary wastewater. Oppenheimer et al. (2011) measured a suite of 85 trace organic and pharmaceutical compounds in a variety of US sanitary wastewaters and concluded that SUC was the best indicator parameter because it was detected in all effluent samples

* Corresponding author. Dept. Earth and Environmental Sciences, University of Waterloo, Waterloo, ON, N2L 3G1, Canada.
*E-mail address:* wroberts@uwaterloo.ca (W.D. Robertson).

http://dx.doi.org/10.1016/j.watres.2015.10.051
0043-1354/

(mean of 27 μg/L, n = 16) and in all surface water samples downstream of wastewater treatment plants (0.12–10 μg/L, n = 11), whereas it was not detected in surface waters where wastewater input was absent (<0.1 μg/L, n = 15). All other compounds, including carbamazepine, were detected less frequently in the wastewater-impacted streams and many were prone to false positives in the non-impacted streams. Acesulfame was not assessed in the above study, however.

Another consideration for SUC is that it is the newest of the commonly used artificial sweeteners, having only been approved for use in the US in 1998 and in the EU in 2003 (Tate and Lyle PLC, 2014). Large scale commercial production of SUC began in 2000 (Tate and Lyle PLC, 2014) and by 2006, it was the largest selling artificial sweetener in the US (Browning, 2007). Thus, over the last decade or so, SUC concentrations in sanitary wastewaters have likely increased considerably. If SUC is as equally mobile and persistent in soils as is ACE, as some laboratory studies suggest (Buerge et al., 2011), then recent increases in SUC concentrations in wastewater could provide a means of providing an approximate age date for wastewater contaminated groundwater, an often problematic task. For example, if a well sample showed evidence of wastewater because of the presence of artificial sweeteners, if the ratio of SUC/ACE was found to be similar to current wastewaters, then the contaminant source may only be a few years old. If the ratio was lower or if SUC was absent, this could indicate older impact originating prior to 2000 in the US or 2003 in the EU, and consequently such a well might be considered less at risk from wastewater-derived contaminants such as pathogens.

In our previous examination of a suite of four artificial sweeteners (acesulfame, sucralose, cyclamate and saccharin) in the Long Point septic system plume, ACE was found to be the most persistent, occurring throughout the 200 m mapped length of the plume (Robertson et al., 2013). Sucralose was also present in concentrations similar to ACE (30–80 μg/L) in the plume proximal zone, but concentrations declined abruptly to close to the method detection limit (5 μg/L at that time), about 70 m from the tile bed in a plume zone that was about 5 yrs old. This zone would have originated around 2005 (sampled in 2010), which is the time frame when SUC use was likely increasing rapidly in Canada (Supporting Material). Although it was previously suggested that the diminished size of the SUC plume at Long Point was evidence of degradation or adsorption (Van Stempvoort et al., 201lb; Robertson et al., 2013), lower historical usage of SUC could have also produced the same effect. Batch tests conducted by LaBare and Alexander (1993) did show degradation of SUC in organic carbon-rich soil and lake bottom sediments (1–17 wt% OC), with 50% removal occurring in about 30–100 days. Much less removal was noted however, in lower carbon, lake water samples (<4% over 80 days, DOC = <50–62 mg/L), and rates were reduced or negligible under anaerobic conditions (LaBare and Alexander, 1993). During these tests, SUC loss was noted immediately, with no lag period, indicating that it was likely cometabolized with other carbon sources.

For the current study, the Long Point septic system plume was resampled and analysed for artificial sweeteners in 2014. This provided a third detailed sampling snapshot over this critical period from 2008 to 2014, shortly after when SUC use was increasing. Examination of concentration trends over this time period should provide insight as to whether the SUC plume at Long Point is dominated by degradation or alternatively, by changing usage patterns. In addition, we analysed septic tank effluent and associated septic system-impacted groundwater, at six other sites in Ontario, Canada, to establish a range of SUC concentrations in typical sanitary wastewater and to examine its persistence in a variety of subsurface environments.

## 2. Study sites

### 2.1. Long Point site

The Long Point (LP) campground, located on the north shore of Lake Erie, has 256 overnight campsites and is open seasonally from mid-May until mid-October. Sewage from a single washroom facility is treated on-site, in a conventional septic system consisting of a septic tank and two separate infiltration beds (tile beds), ~290 $m^2$ each, that receive average wastewater loading of 6 cm/d during the peak use months of July and August. Water limiting fixtures in the washroom result in relatively high concentrations of constituents such as $NH_4^+$-N (100 ± 27 mg/L) and ACE (50 ± 15 μg/L, Robertson et al., 2013) in the wastewater. The groundwater plume from Tile Bed 2 flows southward toward the Lake Erie shoreline within a ~5 m thick unconfined calcareous sand aquifer that is underlain by a clayey silt unit (Fig. 1). In a previous study (Robertson et al., 2013) it was determined that $Cl^-$, $Na^+$ and ACE could be used to map the wastewater plume, although high background $Cl^-$ values in down gradient areas obscured the $Cl^-$ plume there. Except within about 0.5 m of the water table, groundwater throughout the site, both in and outside of the wastewater plume, is sub-oxic (dissolved oxygen (DO) < 1 mg/L, Robertson et al., 2012). In a July 2008 tracer test, NaBr was injected into the septic tank and 290 days later, elevated Br was detected up to 15 m down-gradient from the tile bed (Robertson et al., 2012), indicating a horizontal groundwater velocity of 22 m/yr in the tile bed area. The 200 m-long monitored section of the plume (Fig. 1) is about 15 years old based on tritium/helium age dating undertaken in 2011 (Robertson et al., 2013). Groundwater monitoring in the Tile Bed 2 area has been ongoing since the septic system was commissioned in 1991 (e.g. Aravena and Robertson, 1998; Van Stempvoort et al., 2011b).

### 2.2. Other sites

The other six septic system sites examined in this study are also located Ontario and include two large seasonal-use campgrounds (KP and KR sites), a seasonal-use tourist resort (LJ site), a communal townhouse complex (BU site) and two seasonal-use family cottages (JL and GB sites). All of these septic systems are at least 10 years old and are generally of conventional design, consisting of a septic tank and associated infiltration bed with perforated infiltration pipes installed into the vadose zone at 0.5–1 m depth below ground surface. Two of the sites (family cottage, GB and communal residence, BU) also provide tertiary treatment using aerobic fixed bed filters prior to discharge to the infiltration beds, and the latter site also includes a denitrification module. Most of these are communal systems that receive moderate wastewater loading rates in the range 0.4–6 cm/d during peak use in the summer (July and August). The two family cottage sites (GB and JL) receive slightly lower loading of ~0.3 cm/d during July and August. The effluent at these sites can be considered typical of sanitary wastewater generated in Canada, except that most of these, excluding the townhouse site (BU), are seasonal-use systems that receive highest loading during the summer months. This could influence artificial sweetener concentrations, as there is likely increased consumption of certain food products such as diet soft drinks during the summer. Additional site details are provided in the Supporting Material.

## 3. Methods

### 3.1. Sampling and analyses

In the current study, most sampling occurred from June, 2011–January, 2014, but earlier results from the Long Point site

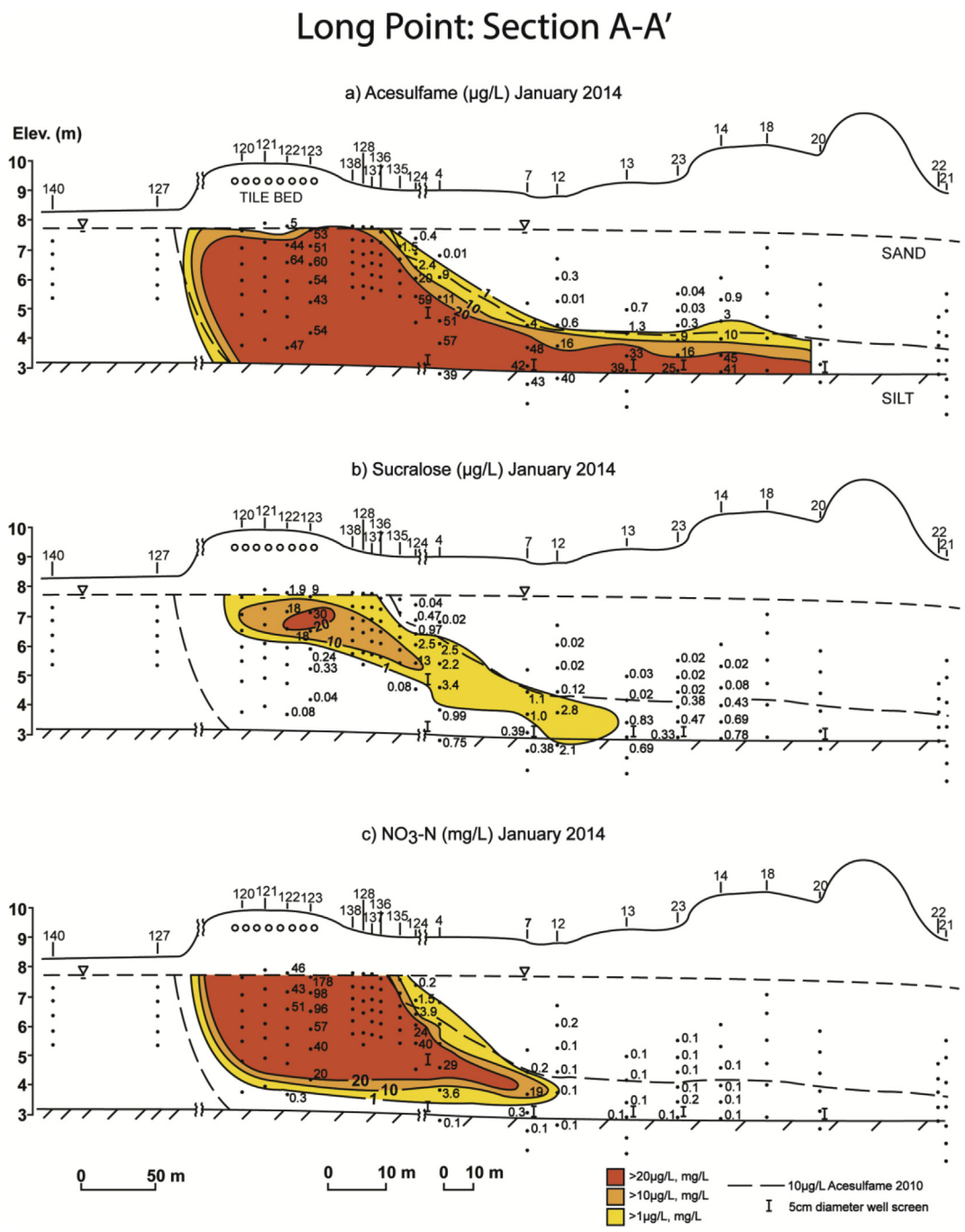


**Fig. 1.** Concentrations of: a) acesulfame, b) sucralose and c) $NO_3^-$-N along the Long Point septic system plume core, Jan. 15, 2014. Open circles in the vadose zone indicate tile bed infiltration pipes.

obtained in September, 2008 and October, 2010 (Van Stempvoort et al., 2011b; Robertson et al., 2013), are also included. Septic tank samples were obtained from dedicated polyethylene sampling tubes installed near the outlet of the tanks, whereas groundwater samples were obtained from multilevel bundle piezometers at most sites. These consisted of from 2 to 6 sampling tubes set at varying depths. At Long Point, SUC concentrations were examined along the entire 200 m mapped length of the plume, whereas at the other six sites results are limited to the tank effluent and the proximal plume zones (immediately below the tile beds within about 1 m of the water table), where in a concurrent study (Robertson et al., 2015), it was established that the plumes, in this zone, were minimally effected by dilution with background groundwater.

Groundwater samples were collected using a peristaltic pump with silicone tubing and were filtered (0.45 µm) in-line, prior to atmospheric exposure. Samples for $NO_3^-$-N and artificial sweeteners were left untreated and were immediately transported to the laboratory where they were either refrigerated at ~ 4° C or frozen (sweetener samples) until analysis. Nitrate was analysed in the Environmental Geochemistry Laboratory (EGL), Department of Earth and Environmental Sciences, University of Waterloo, ON, by ion chromatography using a Dionex ICS-90 (Dionex, Sunnyvale, CA), which provided an analytical reporting limit of <0.1 mg/L $NO_3^-$-N.

Acesulfame and sucralose were analysed at Canada Centre for Inland Waters, Burlington, ON by ion chromatography (Dionex 2500 system) coupled with tandem mass spectrometry (AB Sciex QTRAP 5500 triple-quadrupole), following the methods described by Van Stempvoort et al. (2011a). This technique provided a detection limit of 0.008 μg/L for ACE and 5 μg/L for SUC for samples analysed prior to 2013. System upgrades undertaken in 2013 resulted in lower SUC and ACE detection limits for the 2014 Long Point samples of 0.02 μg/L and 0.002 μg/L, respectively.

## 4. Results and discussion

### 4.1. Variability and persistence of sucralose at Long Point site

Sucralose was present in the septic tank effluent at Long Point at concentrations ranging from 22 to 98 μg/L, except for 5 samples taken shortly after the park was opened in May 2011, when much lower SUC values of <5 μg/L occurred (Table 1). The cause of these abruptly lower values was uncertain. One possibility, is that SUC degraded in the septic tank during the period of disuse from November to May. Acesulfame concentrations in the effluent (32–91 μg/L, Table 1) were generally quite similar to SUC values except during the May 2011 period when ACE remained elevated (36–42 μg/L).

Fig. 1 shows the detailed distribution of SUC along the plume core centreline at Long Point during the most recent sampling event (January, 2014), when it was analysed at the lower detection limit of 0.02 μg/L (compared to 5 μg/L previously). Sucralose concentrations above 1 μg/L occur up to 70 m away from the tile bed (bundle 12), but are limited in depth to about 2 m below the water table in the area below the tile bed. Peak concentrations of 10–30 μg/L occur in this zone. Fig. 1 also shows the distribution of ACE, which was established previously (along with $Na^+$) as the preferred plume tracer (Robertson et al., 2013), and $NO_3^-$-N, which provides an indication of redox conditions present within the plume. Acesulfame occurs throughout the plume core at high concentrations (>25 μg/L) similar to previous sampling in 2010 (Robertson et al., 2013). High $NO_3^-$-N concentrations of up to 178 mg/L are present in the plume proximal zone but these values are depleted to <0.2 mg/L at depth and beyond well 7, located 59 m from the tile bed. Previous studies have established that nitrate at Long Point is biodegraded by both denitrification (Aravena and Robertson, 1998) and anaerobic ammonium oxidation (anammox, Robertson et al., 2012).

Fig. 2 compares depth profiles of both ACE and SUC concentrations at three locations along the plume (LP123 directly below the tile bed, LP4, 28 m from the tile bed and LP7, 59 m from the tile bed) for the three sampling snapshots undertaken between 2008 and 2014. Whereas ACE concentrations remained similar for all three sampling events, SUC behaviour was different, and in fact, concentrations decreased at all three locations in 2014, providing evidence of a shrinking SUC plume. This is contrary what would be expected from increasing usage trends or from sorption related effects, both of which would result in an expanding plume over time. Considering the indicated groundwater velocity of 22 m/yr, the SUC concentrations of ~40 ug/L measured at LP4 in 2010, should have been observed at LP7 in 2014. This was not the case. Other than changing source input (Table 1 indicates that septic tank SUC values remained generally consistent during 2008–2011), degradation is the only process that can restrict plume expansion over time. Furthermore, biodegradation processes have the potential to become more active over time as bacteria populations acclimate to metabolizing specific organic compounds. If the source remained constant, but bacteria populations gradually became more efficient at utilizing this carbon source, the plume would shrink over time. This behaviour provides strong evidence that the SUC plume at Long Point is controlled, foremost, by biodegradation activity rather than by any potential changes in usage trends or sorption-related retardation effects. Comparison of SUC/ACE ratios along the plume core (Fig. 3) shows that ratio values consistent with the effluent occur almost exclusively in or very near the proximal zone, whereas lower values are present throughout the distal plume and at depth in the proximal zone, particularly during sampling in 2014, indicating degradation of SUC. Table 2 gives ratios of ACE and SUC at the three nest locations in 2014, normalized to $Cl^-$ concentrations, which can be used as a conservative tracer. Ratios of ACE/$Cl^-$ in the plume core at all three locations remain near 1.0, close to the mean tank value of 0.65 (Table 2), indicating that ACE behaves conservatively (is not degraded). Ratios of SUC/$Cl^-$, on the other hand, are consistently lower than the mean tank value of 0.95 and become very low in the distal nests (0.01–0.07). These lower ratio values provide further evidence of SUC degradation.

The bulk of the SUC plume at Long Point is contained within the $NO_3^-$-N – rich zone (Fig. 1). This is evident at depth in nest LP123 and in the plume core at LP4 and LP7 where SUC is depleted to ~1 μg/L or less, but $NO_3^-$-N remains >19 mg/L (Fig. 1). Thus, most SUC degradation occurs in the presence nitrate. This zone is suboxic (DO < 1 mg/L) and denitrification is likely active throughout this zone (Aravena and Robertson, 1998), as is indicated by declining $NO_3^-$-N concentrations with depth in nest LP123 (Fig. 1c). This evidence suggests that sucralose might be utilized as a carbon source, or might be co-metabolized with other carbon sources, during denitrification. The previous batch tests of LaBare and Alexander (1993) also suggested co-metabolization of SUC with other carbon sources, because no lag period was noted in their degradation studies.

Approximate age estimates are available for the Long Point groundwater at the three monitoring locations shown in Fig. 2. At LP123 located below the tile bed, a NABr tracer test undertaken in 2008 (Robertson et al., 2012) indicated that groundwater at that location ranged in age from about one month in the shallow zone to about 1 year at 6 m depth. In the plume core at LP4 and LP7, located farther down gradient, tritium/helium age dating undertaken in 2011 (Robertson et al., 2013) indicated age ranges of 2–5 yrs and 4–7 yrs, respectively. It is also important to note that the sampling undertaken in 2014 was done in January, three months after the park was closed for season, whereas previous sampling was done in September and October when the park was still in operation. Thus groundwater ages in the shallow zone at LP123, at 2–3.5 m depth, would have been about one month during sampling in 2008 and 2010 versus about four months during 2014 sampling. Interestingly,

**Table 1**
Concentrations of $Cl^-$ and the artificial sweeteners acesulfame (ACE) and sucralose (SUC) in septic tank effluent at the Long Point (LP) campground during 2008–2011. Note, five samples with low sucralose (<5 μg/L) were collected shortly after the campground was opened for the season on ~May 15, 2011. NA, not available.

| Septic tank effluent | $Cl^-$ (mg/L) | ACE (μg/L) | SUC (μg/L) | SUC/ACE |
|---|---|---|---|---|
| Sept. 11, 2008 | 68 | 61 | 67 | 1.1 |
| Oct. 13, 2009 | 65 | 45 | 95 | 2.1 |
| Aug. 8, 2010 | NA | 60 | 91 | 1.5 |
| Sept. 13, 2010 | NA | 91 | 98 | 1.1 |
| Oct. 4, 2010 | NA | 52 | 92 | 1.8 |
| May 24, 2011 | 81 | 39 | <5 | <0.12 |
| May 27, 2011 | 68 | 41 | <5 | <0.12 |
| May 29, 2011 | 52 | 36 | <5 | <0.14 |
| Jun. 3, 2011 | 56 | 42 | <5 | <0.12 |
| Jun. 8, 2011 | 106 | 41 | <5 | <0.12 |
| Jun. 15, 2011 | 157 | 57 | 86 | 1.5 |
| Jun. 29, 2011 | 135 | 32 | 22 | 0.70 |
| Jul. 8, 2011 | 93 | 55 | 83 | 1.5 |

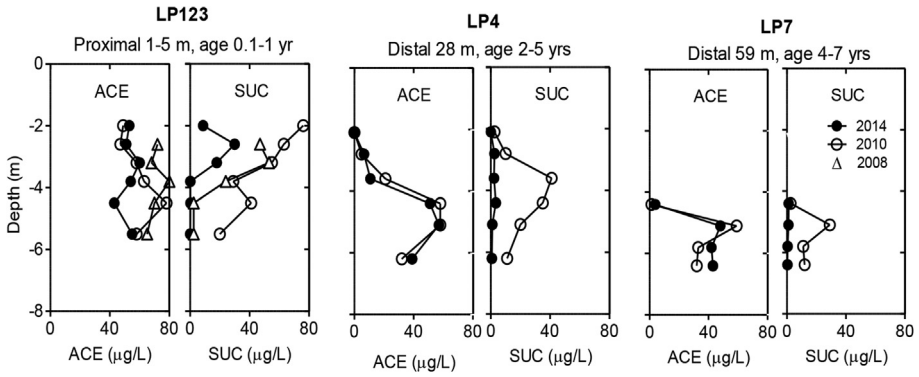


**Fig. 2.** Comparison of ACE and SUC depth profiles at three locations along the plume core during three sampling events: Sept. 11, 2008; Oct. 13, 2010; and Jan. 15, 2014; monitoring bundle LP123, 1–5 m below the tile lines; LP4, 28 m from the tile bed; and LP7, 59 m from the tile bed. Groundwater age is estimated from NaBr tracer breakthrough at LP123 (Robertson et al., 2012) and tritium/helium age dating at LP4 and LP7 (Robertson et al., 2013).

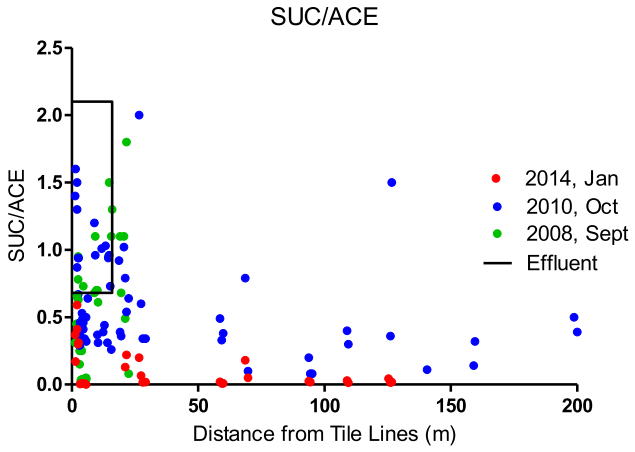


**Fig. 3.** Ratios of SUC/ACE along the core of the plume for three sampling events; Sept. 11, 2008, Oct. 13, 2010 and Jan. 15, 2014. Core zone defined by ACE >8 µg/L; Effluent range is from Table 3 and the width of the box corresponds to the width of the tile bed.

2014 SUC values in this zone (9–30 µg/L, Fig. 2) are about 50% of the values measured in 2008 and 2010 (47–76 µg/L, Fig. 2). Such behaviour is apparently consistent with a SUC half life of about three months in this actively denitrifying environment, reflecting slow degradation over the fall and winter months. The seasonal timing of sampling may have influenced SUC concentrations measured in the proximal zone where the plume is only a few months old, but should have little effect in the distal zone where the plume is several years old. Although Fig. 3 indicates that SUC/ACE ratios have also declined in the distal zone between 2010 and 2014, it is important to note that the 2010 distal zone SUC values were mostly in the range of 5–9 µg/L (Robertson et al., 2013) which was very close to the detection limit of 5 µg/L at that time. Thus, the somewhat higher ratio values observed in the distal zone in 2010, could have been an analytical artifact. The SUC degradation noted at Long Point appears to have occurred over a time frame of a few months to a few years.

### 4.2. Other sites

At the other six septic system sites in Ontario, SUC and ACE values were also compared to Long Point effluent and proximal zone groundwater values (Table 3). The mean SUC and ACE values in effluent at Long Point (57 and 79 µg/L respectively), are higher than mean effluent values at the other sites (7–30 µg/L), with the exception of ACE at the two cottage sites (70–71 µg/L). These relatively high values at Long Point presumably reflect the use of water limiting fixtures in the washroom facility. The mean ratio of SUC/ACE in the proximal zone at Long Point (0.7) is lower than the mean effluent value (1.4) which may be due to SUC degradation in

**Table 2**
Concentrations of $Cl^-$, ACE and SUC and ratios of ACE/$Cl^-$ and SUC/$Cl^-$, in the septic tank effluent and at three well nest locations during sampling on January 15, 2014. Core denotes plume core zone. Septic tank values are mean values from Table 1 (excluding May 24–June 8, 2011 SUC values).

| Well/septic tank | Depth (m) | Plume | $Cl^-$ (mg/L) | ACE (ug/L) | SUC (ug/L) | ACE/$Cl^-$ | SUC/$Cl^-$ |
|---|---|---|---|---|---|---|---|
| Septic tank | | | 88 | 57 | 79 | 0.65 | 0.90 |
| LP123 | 2.0 | Core | 50 | 53 | 8.8 | 1.1 | 0.18 |
| Below tiles | 2.6 | Core | 46 | 51 | 30 | 1.1 | 0.65 |
| | 3.2 | Core | 58 | 60 | 18 | 1.0 | 0.31 |
| | 3.6 | Core | 54 | 54 | 0.24 | 1.0 | 0.004 |
| | 4.5 | Core | 46 | 43 | 0.33 | 0.93 | 0.007 |
| | 5.5 | Core | 49 | 54 | 0.04 | 1.1 | 0.001 |
| LP4 | 2.1 | | 0.55 | 0.01 | <0.02 | 0.02 | <0.036 |
| 28 m from bed | 2.8 | | 12 | 6.5 | 2.5 | 0.53 | 0.20 |
| | 3.6 | | 18 | 10.8 | 2.2 | 0.59 | 0.12 |
| | 4.4 | Core | 46 | 51 | 3.4 | 1.1 | 0.07 |
| | 5.1 | Core | 54 | 57 | 0.99 | 1.1 | 0.02 |
| | 6.2 | Core | 50 | 39 | 0.75 | 0.78 | 0.02 |
| LP7 | 4.4 | | 5.5 | 3.8 | 1.1 | 0.69 | 0.20 |
| 59 m from bed | 5.1 | Core | 50 | 48 | 1.0 | 0.96 | 0.020 |
| | 5.8 | Core | 49 | 42 | 0.39 | 0.86 | 0.008 |
| | 6.4 | Core | 49 | 43 | 0.38 | 0.88 | 0.008 |

**Table 3**
Mean concentrations (±s.d.) of $Cl^-$, ACE and SUC in septic tank effluent (top row) and associated proximal groundwater plumes (bottom row), at seven sites in Ontario, Canada. Brackets indicate range. Five samples from Long Point (LP) effluent with SUC <5 μg/L (May24-Jun. 8, 2011, Table 1) are excluded. "Persons using" is during peak use in July–August for seasonal sites. Additional site information is available in the Supporting Material. Cmp = Campground; Res = Resort; Twn = Townhouse; Cot = Cottage. Sampling occurred during 2012–2013 except 2008–2014 at LP site.

| Site | Wastewater type | Persons using | (n) | $Cl^-$ (mg/L) | ACE (μg/L) | SUC (μg/L) | SUC/ACE |
|---|---|---|---|---|---|---|---|
| LP Cmp | Effluent | 500 | 8 | 88 ± 35 | 57 ± 17 (32–91) | 79 ± 25 (22–98) | 1.4 ± 0.4 (0.7–2.1) |
| | Prox. plume | | 20 | 54 ± 11 | 59 ± 21 (5–99) | 40 ± 23 (2–77) | 0.7 ± 0.4 (0.2–1.6) |
| KP Cmp | Effluent | 250 | 3 | 21 ± 3 | 21 ± 3 (19–25) | 15 ± 3 (12–18) | 0.7 ± 0.2 (0.6–1.0) |
| | Prox. plume | | 22 | 32 ± 8 | 18 ± 3 (12–24) | 10 ± 2 (7–12) | 0.6 ± 0.1 (0.4–0.7) |
| KR Cmp | Effluent | 240 | 4 | 33 ± 5 | 21 ± 8 (16–25) | 12 ± 2 (11–14) | 0.6 ± 0.2 (0.3–0.9) |
| | Prox. plume | | 8 | 26 ± 11 | 13 ± 7 (10–22) | 11 ± 4 (6–19) | 0.7 ± 0.1 (0.5–0.9) |
| LJ Res | Effluent | 85 | 5 | 138 ± 22 | 14 ± 7 (6–22) | 7.1 ± 1.5 (6–9) | 0.7 ± 0.3 (0.4–1.1) |
| | Prox. plume | | 8 | 111 ± 36 | 6 ± 4 (1–16) | 4 ± 3 (0.7–10) | 0.6 ± 0.2 (0.4–0.7) |
| BU Twn | Effluent | 70 | 7 | 332 ± 51 | 18 ± 2 (15–22) | 7.9 ± 1.2 (6–9) | 0.4 ± 0.1 (0.3–0.6) |
| JL Cot | Effluent | 3 | 3 | 63 ± 18 | 70 ± 30 (48–103) | 30 ± 7 (26–38) | 0.5 ± 0.4 (0.3–0.7) |
| | Prox. plume | | 1 | 27 | 38 | 22 | 0.6 |
| GB Cot | Effluent | 3 | 2 | 43 ± 1 | 71 ± 20 (57–85) | 10 ± 1 (9–11) | 0.2 ± 0.1 (0.1–0.2) |
| | Prox. plume | | 5 | 51 ± 23 | 59 ± 37 (22–117) | 9 ± 2 (7–10) | 0.1 ± 0.0 (0.1–0.1) |

the proximal zone. However, such a difference is not as evident at the other sites, where SUC/ACE ratios remain similar in both the effluent and proximal plume zones, indicating persistence of SUC. Mean ratio values at five of the other sites remain within a relatively small range (0.4–0.7) whereas lower mean ratios were observed at one site (GB cottage) in both the effluent and plume water (0.1–0.2). A broader range of values is to be expected in individual household or cottage wastewaters because of varying dietary consumption of artificial sweeteners among individuals, whereas communal systems are more likely to reflect average values. Additionally, it should be noted that all of the these sites except the communal residence, are seasonal-use sites that generate wastewater primarily during the summer months. Thus, there could be seasonal effects such as relatively higher consumption of diet soft drinks at these sites, which could increase concentrations or change concentration ratios of the artificial sweeteners compared to wastewater generated during other seasons.

These plumes encounter a range of sediment types and redox environments and thus provide examples of SUC persistence in subsurface environments that are different than Long Point. Sediments at the LP, KP, KR and LJ sites are predominantly sand, whereas clay and silt are present at the JL and GB sites (Supporting Materials). The proximal plume at LJ is aerobic, whereas suboxic conditions are present at KP, KR and GB sites and declining $NO_3^-$ concentrations at the LP, JL and BU sites indicate that denitrifying conditions occur (Supporting Materials).

All samples of septic tank effluent from the seven sites (n = 32) had SUC > 6 μg/L and all samples from the proximal groundwater zones had SUC > 0.7 μg/L (n = 64). Unlike Long Point, where estimates of groundwater age are available from tracer tests and tritium/helium dating, no direct estimates of groundwater age are available at the other sites. However, considering the location of the proximal zone sampling points, (directly below the tile beds within about 1 m below the water table) and considering effluent loading rates and site hydrogeological conditions, it is likely that these samples represent groundwater that ranges in age from a few weeks to about one year. The persistence of SUC in the groundwater plumes at all of these sites demonstrates that if degradation is occurring, rates are sufficiently slow such that large percentage reductions are not evident in the proximal zones (with the possible exception of Long Point) over a time frame of several months or so.

### 4.3. Comparison to previous studies

Our study demonstrates that, for seven septic systems typical of those found in Canada, SUC concentrations in sanitary wastewater (6–98 μg/L) are consistently about 500 times higher than background detection limit values (0.02 μg/L). These data suggest that SUC is likely ubiquitous in Canadian sanitary wastewater, making it an excellent wastewater tracer. Our measured concentrations are in the same range as values reported for septic tank effluent in the US (12–80 μg/L at eight sites, Oppenheimer et al., 2011), but are somewhat higher than values reported for municipal sewage in some parts of the world, for example mean of 27 μg/L in six US sewage treatment plants (STPs), 2–10 μg/L in 10 Swiss STPs, 0.5–1.5 μg/L in five German STPs and 2–10 μg/L in ~60 Swedish STPs (Lange et al., 2012). Generally lower values in European wastewaters could reflect the more recent approval of SUC for use in the EU (2003) compared to its earlier introduction in the US and Canada (2000) or could reflect different usage patterns in these markets. Lange et al. (2012) and Subedi and Kannan (2014) also compared influent and effluent values for the European and US STPs noted above and found minimal removal of both SUC and ACE, whereas other artificial sweeteners such as saccharin and cyclamate were substantially removed.

The persistence of SUC and ACE during sewage treatment has been well documented (Lange et al., 2012) and some laboratory flow-through column tests have found SUC to be equally mobile and persistent as ACE in some sediments (Buerge et al., 2011). These column tests had hydraulic retention times of only a few days however, much shorter than the multiyear timescales associated with the Long Point plume. Buerge et al. (2011) also conducted longer term laboratory batch tests using a suite of relatively carbon-rich soil samples (1–18 wt% organic carbon (OC)) and then noted degradation of both SUC and ACE under aerobic conditions, at half lives in the range of 8–124 and 3–49 days respectively. These results were similar to the earlier batch tests of LaBare and Alexander (1993) that also examined SUC degradation in OC rich soils, but which also included testing in lower DOC lake water samples as well. Sucralose degradation observed in the Long Point plume appears generally consistent with these previous laboratory observations. The proximal plume zone at Long Point is a low organic carbon environment (0.15 wt% OC, DOC ~5 mg/L, Aravena and Robertson, 1998). Thus, the slow depletion of SUC over a period of several months to several years is reasonably consistent with the lower removal rates (<4% over 80 days) observed by LaBare and Alexander (1993) in their low DOC lake samples. Although the proximal plume zone where most SUC depletion occurs is suboxic (<1 mg/L DO), high nitrate values are present and a number facultative aerobic bacteria would likely be capable of utilizing nitrate as an electron acceptor. It is noted that in the more distal

plume zone where nitrate is depleted (beyond nest LP 7), SUC persisted at 0.5–2 μg/L during sampling in 2014, which was well above the detection limit of 0.02 ug/L (Fig. 1). This suggests that degradation rates may have diminished in this more anaerobic zone.

There are relatively few studies that document SUC persistence in groundwater flow systems. Scheurer et al. (2011) noted lower SUC concentrations in perimeter monitoring wells located around a large sewage infiltration bed in Israel and concluded this was evidence for degradation, as other sewage markers such as ACE and carbamazepine had concentrations that remained similar to the sewage. Our study supports this earlier evidence of SUC degradation in groundwater, but also our screening of multiple sites shows that it has the capacity to persist over timeframes of several months to several years in many groundwater environments.

### 4.4. Implications for groundwater age dating

Knowing what changes in artificial sweetener use have occurred over time is potentially helpful for determining the approximate age of wastewater-impacted groundwater. Roy et al. (2014) assessed leachate and contaminated groundwater from 15 active and legacy landfill sites in Canada, and found that at landfills that were decommissioned prior to the mid-1990s, saccharin was the dominant artificial sweetener, and was present at the μg/L range, whereas ACE was much lower or was not detected. This pattern was much different in active landfills where ACE concentrations approached or exceeded saccharin levels. Saccharin has been in use in Canada for over half a century, whereas ACE was not introduced until 1988 (Roy et al., 2014). The even more recent introduction of SUC (~2000 in Canada), could further add to the potential of using relative artificial sweetener abundances as a tool for constraining groundwater age.

The Long Point data clearly show the susceptibility of SUC to slow degradation in some groundwater environments. However, it persists in the plume at concentrations >1 μg/L for several years, and this value is still 50 times above the current detection limit of 0.02 μg/L. At the other six sites, SUC was present in all samples of septic tank effluent and was found in the proximal zone groundwater plumes at concentrations similar to the effluent (Table 3), and this groundwater likely ranged in age from few weeks to about one year. Degradation estimates are not provided for these other sites because monitoring was limited to the proximal zones where groundwater was relatively young. However, an absence of declining SUC concentrations in the proximal zones at all of these sites, indicates that if degradation is occurring, it occurs slowly, likely not substantially faster than the rate observed at Long Point, where degradation with a half life of a few months or so was indicated. Thus, if a well is impacted by sanitary wastewater contamination and travel times from the source to the well are less than several years, it appears likely that both ACE and SUC would be present and at ratios similar to values observed in this study (0.1–1.5, Table 3). Such wells might be deemed relatively more vulnerable, to pathogen risk for example, compared to other wells where ACE was present but SUC absent, suggesting the contaminant source had likely experienced a travel time of more than several years. Tritium/helium age dating is currently the only dating technique, commonly used, that is capable of identifying groundwater that is only a few years old (Solomon and Cook, 2000), yet this is the time frame that is often most critical when attempting to assess well vulnerability to contamination. More work should be done investigating SUC (and ACE) persistence in groundwater environments, so that use of artificial sweetener ratios might be further explored as a potential tool for constraining age estimates of wastewater-contaminated groundwater. This work should include studies of aerobic plumes, where laboratory studies have indicated that rates of SUC (and ACE) degradation could be higher and should include expanded monitoring in distal plume zones where older aged groundwater would be encountered.

## 5. Conclusions

The series of three sampling snapshots undertaken at the Long Point septic system plume during 2008–2014, clearly show that SUC concentrations are not increasing in response to recent increased consumption, but rather the plume is shrinking. The mean SUC concentration of 40 μg/L in the proximal plume zone decreases to ~1 μg/L after plume travel times of about 1–7 years, whereas other plume indicators, such as ACE, remain consistently high throughout this zone. This indicates degradation of SUC, but at a relatively slow rate. Furthermore, sampling of six other septic system sites in Ontario revealed the ubiquitous presence of SUC in both the septic tank effluent and proximal groundwater plumes at concentrations >0.7 μg/L. The ubiquitous presence of SUC in sanitary wastewater in Canada and elsewhere, combined with its relatively recent introduction (2000–2003) and slow rate of degradation in many groundwater environments, opens up the possibility of using this compound to fingerprint 'recent' sources of sanitary wastewater contamination in groundwater.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2015.10.051.

## References


Aravena, R., Robertson, W.D., 1998. Use of multiple isotope tracers to evaluate denitrification in ground water: study of nitrate from a large-flux septic system plume. Groundwater 36 (6), 975–982.

Browning, L., 2007. Makers of artificial sweeteners go to court. Wall Str. J. 9, 2015. April 6, 2007, Business Section; accessed February.

Buerge, I.J., Buser, H.R., Kahle, M., Müller, M.D., Poiger, T., 2009. Ubiquitous occurrence of the artificial sweetener acesulfame in the aquatic environment: an ideal chemical marker of domestic wastewater in groundwater. Environ. Sci. Technol. 43 (12), 4381–4385.

Buerge, I.J., Keller, M., Buser, H.R., Müller, M.D., Poiger, T., 2011. Saccharin and other artificial sweeteners in soils: estimated inputs from agriculture and households, degradation, and leaching to groundwater. Environ. Sci. Technol. 45 (2), 615–621.

Clara, M., Strenn, B., Kreuzinger, N., 2004. Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of Carbamazepine in wastewater treatment and during groundwater infiltration. Wat. Res. 38, 947–954.

LaBare, M.P., Alexander, M., 1993. Biodegradation of sucralose, a chlorinated carbohydrate, in samples of natural environments. Environ. Chem. 12, 797–804.

Lange, F.T., Scheurer, M., Brauch, H.J., 2012. Artificial sweeteners-a recently recognized class of emerging environmental contaminants: a review. Anal. Bioanal. Chem. 403, 2503–2518.

Mawhinney, D.B., Young, R.B., Vanderford, B.J., Borch, T., Snyder, S.A., 2011. Artificial sweetener sucralose in U.S. drinking water systems. Environ. Sci. Technol. 45, 8716–8722.

Oppenheimer, J.A., Eaton, A., Badruzzaman, M., Hagnani, A.W., Jacangelo, J.G., 2011. Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in urbanized regions. Water Res 45, 4019–4027.

Robertson, W.D., Moore, T., Spoelstra, J., Li, L., Elgood, R., Clark, I.D., Schiff, S.L., Aravena, R., Neufeld, J.D., 2012. Natural attenuation of septic system nitrogen by anammox. Groundwater 50 (4), 541–553.

Robertson, W.D., Van Stempvoort, D.L., Solomon, D.K., Homewood, J., Brown, S.J., 2013. Persistence of artificial sweeteners in a 15-year-old septic system plume. J. Hydrol. 477, 43–54.

Robertson, W.D., Van Stempvoort, D.R., Roy, J.W., Brown, S.J., Spoelstra, J., Schiff, S.L., Rudolph, D.R., Danielescu, S., Graham, G., 2015. Use of an artificial sweetener to identify sources of groundwater nitrate contamination. Groundwater submitted Mar. 2015.

Roy, J.W., Van Stempvoort, D.R., Bickerton, G., 2014. Artificial sweeteners as potential tracers of municipal landfill leachate. Environ. Pollut. 184, 89–93.

Scheurer, M., Storck, F.R., Graf, C., Brauch, H.J., Ruck, W., Lev, O., Lange, F.T., 2011. Correlation of six anthropogenic markers in wastewater, surface water, bank filtration, and soil aquifer treatment. J. Environ. Monit. 13, 966–973.

Schmid Neset, T.S., Singer, H., Longree, P., Bader, H.P., Scheidegger, R., Wittmer, A., Andersson, J.C.M., 2010. Understanding consumption-related sucralose emissions - a conceptual approach combining substance-flow analysis with sampling analysis. Sci. Total Environ. 408, 3261–3269.

Solomon, D.K., Cook, P.G., 2000. $^{3}$H and $^{3}$He. In: Cook, P.G., Herezeg, A.L. (Eds.), Environmental Tracers in Subsurface Hydrology. Kluwer Academic Publishers. ISBN 0-7923-7707-9.

Spoelstra, J., Schiff, S.L., Brown, S.J., 2013. Artificial sweeteners in a large Canadian river reflect human consumption in the watershed. PLoS One 8 (12), e82706. http://dx.doi.org/10.1371/journal.pone.0082706.

Subedi, B., Kannan, K., 2014. Fate of artificial sweeteners in wastewater treatment plants in New York State, U.S.A. Environ. Sci. Technol. 48, 13668–13674.

Tate and Lyle PLC, 2014. Interim Management Statement. Press release, Feb. 13, 2014. (accessed 01.02.15.).

Tran, N.H., Hu, J., Li, J., Ong, S.L., 2014. Suitability of artificial sweeteners as indicators of raw wastewater contamination in surface water and groundwater. Wat. Res. 48, 443–456.

Van Stempvoort, D.R., Brown, S.J., Roy, J.W., Bickerton, G., 2011a. Artificial sweeteners as potential tracers in groundwater in urban environments. J. Hydrol. 401 (1–2), 126–133.

Van Stempvoort, D.R., Robertson, W.D., Brown, S.J., 2011b. Artificial sweeteners in a large septic plume. Groundwat. Monit. Remediat. 31 (4), 95–102.

Van Stempvoort, D.R., Roy, J.W., Brown, S.J., Bickerton, G., Sverko, E., 2013. An artificial sweetener and pharmaceutical compounds as co-tracers of urban wastewater in groundwater. Sci. Total Environ. 461–462, 348–359.

Wolf, L., Zwiener, C., Zemann, M., 2012. Tracking artificial sweeteners and pharmaceuticals introduced into urban groundwater by leaking sewer networks. Sci. Total Environ. 403, 8–19.