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Artificial sweeteners as potential tracers of municipal landfill leachate

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ABSTRACT

Artificial sweeteners are gaining acceptance as tracers of human wastewater in the environment. The 3 artificial sweeteners analyzed in this study were detected in leachate or leachate-impacted groundwater at levels comparable to those of untreated wastewater at 14 of 15 municipal landfill sites tested, including several closed for >50 years. Saccharin was the dominant sweetener in old (pre-1990) landfills, while newer landfills were dominated by saccharin and acesulfame (introduced 2 decades ago; dominant in wastewater). Cyclamate was also detected, but less frequently. A case study at one site illustrates the use of artificial sweeteners to identify a landfill-impacted groundwater plume discharging to a stream. The study results suggest that artificial sweeteners can be useful tracers for current and legacy landfill contamination, with relative abundances of the sweeteners potentially providing diagnostic ability to distinguish different landfills or landfill cells, including crude age-dating, and to distinguish landfill and wastewater sources.

1. Introduction

Over the past several years artificial sweeteners have been proposed and demonstrated as useful tracers of domestic and municipal wastewater in the environment (e.g. Buerge et al., 2009, 2011; Scheurer et al., 2009, 2011; Müller et al., 2012; Oppenheimer et al., 2011; Van Stempvoort et al., 2011a), including wastewater plumes in groundwater (Van Stempvoort et al., 2011b). Indeed, Buerge et al. (2009) suggested that the artificial sweetener acesulfame fits the requirements of an ideal marker for the detection of wastewater given its widespread occurrence, its recalcitrance to microbial degradation, and its conservative transport in surface and groundwater. Two other artificial sweeteners, saccharin and cyclamate, have also been detected in surface waters (Buerge et al., 2009; Scheurer et al., 2009) and in various groundwaters (Van Stempvoort et al., 2011a), associated with wastewater sources. Further details on artificial sweeteners in the environment are provided in the review by Lange et al. (2012).

While wastewater sources have been the focus of most of the environmental investigations involving artificial sweeteners, a few non-wastewater sources have also been reported. For example, saccharin is a known soil metabolite of certain sulfonylurea herbicides (Roberts and Hutson, 1998), and thus may leach to groundwater with infiltration from agricultural fields. In addition, Buerge et al. (2011) identified saccharin as a feed-additive for pigs and reported its detection in pig manure. Lesser amounts of saccharin are used industrially as a nickel electroplating brightener, chemical intermediate, and anaerobic adhesive accelerator (Mitchell and Pearson, 1991).

Van Stempvoort et al. (2011a) suggested another potential source of artificial sweeteners in the aquatic environment following the detection of high levels of saccharin but low levels of acesulfame in shallow groundwater discharging to an urban stream (~400 m section) in Barrie, ON. This was an unexpected pattern based on previous studies on artificial sweeteners in the environment (see references above). Rather than being associated with wastewater, or pesticide or pig manure sources, they judged that the source of this saccharin was an old landfill adjacent to this section of stream. In this case, the groundwater containing the saccharin also had other contaminants that are commonly found in landfill leachate, such as ammonium, salts, and various organic chemicals.

The various solid and liquid wastes (e.g. food wastes) placed in municipal landfills could be significant sources of artificial sweeteners to landfill leachate. However, information on the occurrences and relative abundances of the different artificial sweeteners in landfill leachate is unavailable. This information is urgently required to inform the use of artificial sweeteners as tracers of wastewater, given that both types of contaminant sources may occur in similar areas (i.e. near human civilizations) and that landfill leachate is commonly collected and disposed to wastewater treatment plants. Such information would also reveal the potential

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Table 1
Artificial sweeteners detected in leachate or groundwater samples from various landfill sites across Canada.

Landfill	Lifespan	No. samples; sample type	Maximum acesulfame (μg/L)	Maximum saccharin (μg/L)	Maximum cyclamate (μg/L)
Regina	1961–present	2; wells	32	87	n.d.
Thunder Bay	1993–present	2; leachate	0.5	18	n.d.
Cambridge	1973–2003	3; wells	12	25	4.8
Hamilton – Glanbrook	1979–present	4; wells	11	1.2	n.d.
		1; leachate	8.6	3.0	n.d.
Hamilton – Binbrook	1950s–1980	6; wells	n.d.	<l.q.	n.d.
Hamilton – West Hamilton	1955–1977	10; wells	0.2	3.3	0.5
Waterloo	1986–present	6; wells	3.7	16	2.1
Fredericton	1987–present	2; pond and leachate	82	n.d.	n.d.
Hamilton – Rennie	1950–1971	4; wells	0.6	0.5	n.d.
Hamilton – Ancaster	1960–1982	5; wells	n.d.	250	0.9
Terrebonne	1982–present	1; leachate	59	0.5	n.d
Oakville (Halton)	1992–present	1; leachate	85	1.6	n.d.
Jasper	1970–1994	8; wells	0.05	11	14
Barrie – Dyments Creek	1960–1963	90; drive-point	0.3	17	1.1
Barrie – Bunkers Creek	1947–1964	8; drive-point	0.3	3.1	n.d.

n.d. = non-detection; l.q. = limit of quantitation.

value in using artificial sweeteners for identifying and tracking impacts from landfills on groundwater and surface waters. Therefore, the objective of this study was to investigate the occurrence of artificial sweeteners in municipal landfill leachate and discuss their potential use as landfill tracers, specifically in groundwater.

For this work we collected water samples of leachate or leachate-impacted groundwater at 15 different landfill sites across Canada and analyzed these for three commonly-detected artificial sweeteners – acesulfame, saccharin, and cyclamate. These landfills represent a wide spectrum of ages, city sizes and geographic locations (Fig. S1), including a range of lifespans from those that have been closed for decades to those recently opened (Table 1). The idea was to use this survey-scale sampling to ascertain whether these sweeteners persist in the leachate/local impacted groundwater environment at significant levels such that they could serve as tracers for municipal landfill leachate. At one site (Jasper, Alberta), artificial sweeteners were used to track a landfill leachate groundwater plume to a nearby stream, to illustrate the potential of the artificial sweeteners as landfill tracers.

There is potential that the relative composition of the different artificial sweeteners, reflecting the use history of these chemicals, could help to distinguish different landfill sources. For example, in Canada acesulfame has been in use for only about two decades (Gougeon et al., 2004), while saccharin and cyclamate were introduced over a half-century ago. However, in the 1970s, saccharin and cyclamate were de-listed as food additives in Canada, although restricted access to them, such as for use as a table-top sweetener and a non-medicinal chemical ingredient found in certain drug products, was maintained. While this study focuses on landfills in Canada, the general findings should be broadly applicable, even though relative occurrences would depend on the history of sweetener uses in individual countries. Some of the history of sweetener use is shared globally because acesulfame was discovered in 1967, and its first global approval was in 1983 (http://www.acesulfamek.org/approval.html).

2. Methods

The majority of samples were collected from leachate collection systems and/or monitoring wells owned or operated by landfill operators. We refer to these samples as "leachate" and "groundwater" respectively. The wells were either within or immediately adjacent to the landfill cells (see Table 1 for details). For ten of the sites, samples were collected for us by landfill operators and shipped to us. For three of the sites, well samples were collected and transported by us directly. At one of these sites (Jasper), additional shallow groundwater samples (~0.25–0.75 m depth) were collected with a drive-point sampler (see Roy and Bickerton, 2010; for details) along a short stream that drains a wetland into a side channel of the Athabasca River, about 400–500 m from the landfill (Fig. 2). A few surface water samples were also collected here. For the two sites in Barrie, shallow groundwater was collected with this same drive point sampler along sections of small urban streams that were directly adjacent to old shallowly-buried landfill material (i.e. dumps). One of these stream sites (Dyment Creek) has been documented previously (Van Stempvoort et al., 2011a; Roy and Bickerton, 2012).

Analysis of artificial sweeteners was performed using a Dionex (Sunnyvale, CA, USA) 2500 ion chromatography (IC) system coupled to a QTRAP 5500 (AB Sciex, Concord, ON, CAN) triple quadrupole tandem mass-spectrometer, which was operated in negative electrospray ionization (ESI) mode. Filtered water samples were injected onto the IC system, with a potassium hydroxide gradient eluent run from 10 to 75 mM at a flow rate of 0.35 mL min^{-1}. The IC effluent was then combined with 0.2 mL min^{-1} of methanol via a 1200 series Agilent (Santa Clara, CA, USA) isocratic pump, to give a total flow of 0.55 mL min^{-1} to the mass spectrometer. Two multiple reaction monitoring (MRM) transitions were monitored for each analyte and one for each isotope-labeled internal standard. High purity chemicals and isotope-labeled internal standards were used. Full details of this analytical method are provided by Van Stempvoort et al. (2011a; supporting information). The minimum detection limits and practical quantification limits were 8 and 20 ng L^{-1} for acesulfame, 21 and 60 ng L^{-1} for saccharin, and 3 and 10 ng L^{-1} for cyclamate, respectively. See Roy and Bickerton (2012) for details on the major ions and volatile organic compound analyses for the Jasper site.

3. Results and discussion

3.1. Landfills survey

Artificial sweeteners were detected in leachate or groundwater samples from nearly all of the 15 sites (Table 1), which include landfills currently receiving municipal waste, but also those that have been closed for decades (up to a half century). Only trace levels (below limits of quantification) were found at the Hamilton – Binbrook site. Here, none of the six sampled wells were within the landfill proper, so it is possible that elevated levels exist at the site but were missed. Alternately, it may be that sweeteners were once present in this landfill but did not persist, perhaps flushed out long ago given that this is one of the oldest landfill sites (1950s to 1980). Despite this outlier site, the results indicate that artificial sweeteners are common components of landfill leachate and that they can persist within landfills for decades.

Saccharin was the most abundant sweetener detected; it was only missing from one (Fredericton) of the 14 sites with quantifiable levels of artificial sweeteners (Table 1). Acesulfame was the next most abundant (11 sites at >0.1 μg L^{-1}), with cyclamate only occurring at 5 sites. The low frequency of detection for cyclamate may be a result of several factors, including lower usage rates or greater degradation in the subsurface. These findings suggest that