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ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · JANUARY 2011

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Saccharin and Other Artificial Sweeteners in Soils: Estimated Inputs from Agriculture and Households, Degradation, and Leaching to Groundwater

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Received September 14, 2010. Revised manuscript received
November 22, 2010. Accepted November 23, 2010.

Artificial sweeteners are consumed in substantial quantities as sugar substitutes and were previously shown to be ubiquitously present in the aquatic environment. The sweetener saccharin is also registered as additive in piglet feed. Saccharin fed to piglets was largely excreted and, consequently, found in liquid manure at concentrations up to 12 mg/L, where it was stable during 2 months of storage. Saccharin may thus end up in soils in considerable quantities with manure. Furthermore, other studies showed that saccharin is a soil metabolite of certain sulfonyleurea herbicides. Sweeteners may also get into soils via irrigation with wastewater-polluted surface water, fertilization with sewage sludge (1–43 $\mu\text{g/L}$), or through leaky sewers. In soil incubation experiments, cyclamate, saccharin, acesulfame, and sucralose were degraded with half-lives of 0.4–6 d, 3–12 d, 3–49 d, and 8–124 d, respectively. The relative importance of entry pathways to soils was compared and degradation and leaching to groundwater were evaluated with computer simulations. The data suggest that detection of saccharin in groundwater (observed concentrations, up to 0.26 $\mu\text{g/L}$) is most likely due to application of manure. However, elevated concentrations of acesulfame in groundwater (up to 5 $\mu\text{g/L}$) may result primarily from infiltration of wastewater-polluted surface water through stream beds.

Introduction

Recent studies have documented the widespread occurrence of artificial sweeteners in the aquatic environment (1–5). Sweeteners are consumed in considerable quantities with low-calorie food and beverages. Hence, four compounds were consistently detected in domestic wastewater at concentrations of several $\mu\text{g/L}$. Acesulfame and sucralose were not eliminated in wastewater treatment plants (WWTPs), whereas cyclamate and saccharin were readily biodegraded but were still detectable in treated wastewater. Consequently, the four sweeteners were also found in surface waters receiving discharges from WWTPs. Moreover, acesulfame was detected in a large number of groundwater samples (2). High concentrations up to 5 $\mu\text{g/L}$ were observed in areas with

known, significant infiltration of river water. Acesulfame was found to be a suitable chemical marker of domestic wastewater in natural waters (2, 6).

Artificial sweeteners may also end up in the terrestrial environment through various pathways (Figure 1). Wastewater-polluted surface water may be used for irrigation of agricultural fields (7, 8). In certain countries, digested sewage sludge is applied as fertilizer in agriculture (9, 10). Furthermore, untreated wastewater may seep into subsoils through leaky sewers.

Human consumption is not the only source of sweeteners in the environment. In many countries, including Switzerland, saccharin is also registered as additive in piglet feed, and the compound may get into agricultural soils via application of manure. Saccharin is also a major soil metabolite of certain sulfonyleurea herbicides (metsulfuron-methyl, tribenuron-methyl, propoxycarbazone (11)).

In this study, the relative importance of various entry pathways of artificial sweeteners to soils and further to groundwater was assessed. For this purpose, we determined levels of saccharin in pig manure and studied the degradation during storage. We also analyzed acesulfame, cyclamate, saccharin, and sucralose in a number of sewage sludge samples. The amounts of sweeteners reaching topsoils via application of manure and sewage sludge were estimated and compared with possible inputs via irrigation and herbicide application/transformation.

Degradation of sweeteners in soils was then studied with batch incubation experiments. Transport from soils to groundwater was finally evaluated with computer simulations. Simulated concentrations in groundwater from this pathway were compared to measured concentrations stemming from inputs via infiltration of wastewater-polluted surface water through stream beds. We also conducted a column leaching experiment with untreated domestic wastewater and subsoil material aimed at reproducing the situation of a leaky sewer.

Experimental Section

Chemicals. Acesulfame K (6-methyl-1,2,3-oxathiazin-4(3H)-one-2,2-dioxide potassium salt, purity, 99%), N-cyclohexylsulfamic acid (98%), and saccharin (1,2-benzisothiazol-3(2H)-one-1,1-dioxide, 99%) were from Fluka, Buchs, Switzerland, sucralose (1,6-dichloro-1,6-dideoxy- β -D-fructofuranosyl-4-chloro-4-deoxy- α -D-galactopyranoside, 99.6%) from Chem-os, Regenstauf, Germany, and sucralose-d₆ (98%), used as

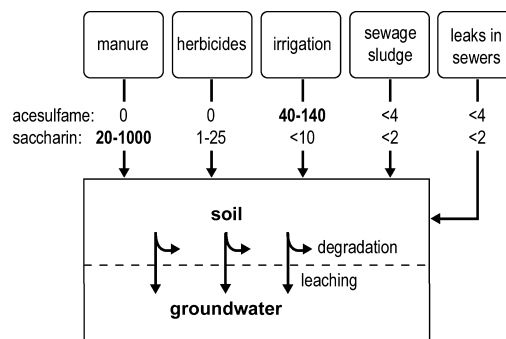


FIGURE 1. Selected entry pathways of artificial sweeteners to soils and further to groundwater. Estimated annual inputs of acesulfame and saccharin to soils in g/ha (assumptions, see Results and Discussion). An additional, important input pathway into groundwater is infiltration of wastewater-polluted surface water through stream beds (not shown, see text).

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TABLE 1. Sampling Sites, Soil Characterization, and Half-Lives of Artificial Sweeteners in Soils

soil site	altitude [m]	texture	C _{org} [%]	pH (CaCl ₂) ^a	moisture [%] ^b	acesulfame DT ₅₀ [d] ^c	cyclamate DT ₅₀ [d] ^c	saccharin DT ₅₀ [d] ^c	sucralose DT ₅₀ [d] ^c
Dübendorf, arable land	440	loam	1.9	7.2	24/37	19/9.3	2.0/0.98	8.9/4.4	11/5.3
Ins, arable land	433	clay loam	7.3	7.1	40/44	17/9.3	2.1/1.2	8.7/4.9	12/6.5
Zuzwil, arable land	557	loam	1.2	7.5	22/44	49/27	5.7/3.2	4.0/2.3	8.2/4.6
Ebikon, fertilized meadow	635	loam	3.0	6.8	27/34	3.2/1.5	0.44/0.21	3.3/1.6	9.2/4.3
Entlebuch, fertilized meadow	955	sandy loam	4.2	5.5	47/40	7.9/4.2	1.2/0.64	3.6/1.9	17/8.7
Realp, alpine pasture	2120	clay	18	4.0	174/60	5.2/3.6	1.1/0.78	12/8.2	124/87
Ebikon, sterilized soil	635	loam	3.0	6.8	27/34	— ^d	21/10	— ^d	— ^d
geometric mean ^e						11/6.1	1.6/0.84	5.9/3.3	16/9.0

^a Suspension of soil in 0.01 M CaCl₂, 1:2.5 (w/w). ^b In g water per 100 g dry soil/in % of the maximum water holding capacity. ^c Time to 50% dissipation, DT₅₀, obtained with a first-order kinetic model. Experimentally determined value/normalized value to 100% field capacity using the Walker equation with an exponent of 0.7 (20). ^d No degradation observed during 61 d of incubation. ^e Sterilized soil excluded.

TABLE 2. Concentrations of Saccharin in Piglet Feces, Liquid Pig Manure, and Manure from a Fermentation Plant^e

farm no.	sampling date (2009)	piglet feces	pH	dry weight [%]	saccharin [mg/kg] ^c	
1	April 30	piglets fed with saccharin ^a	7.7 ^b	28	260	
	May 11	piglets fed with saccharin ^a	nd ^f	23	260	
	May 18	piglets fed with saccharin ^a	nd ^f	25	240	
farm no.	sampling date (2009)	liquid manure	pH	dry weight [%]	saccharin [mg/L]	acesulfame [mg/L]
1	May 11	20 piglets fed with saccharin ^a , 65 piglets fed without saccharin, 130 sows, 265 porkers	7.1	1.4	0.3	<0.001
	May 18		7.9	0.8	0.3	<0.001
2	September 01	≈150 piglets, 70 sows, rainwater (open manure pit)	7.1	0.6	0.8	<0.001
3	September 01	240 piglets, 160 suckling piglets, 106 sows	7.3	1.2	1.0	<0.001
4	July 30	≈90 piglets, wastewater from a 6-persons household	7.6	0.8	3.2	0.048
5	July 30	60–70 piglets, 30 sows, some rainwater	7.8	0.5	6.3	<0.001
6	September 01	55 piglets, 5 sows	7.3	2.0	12	<0.001
manure fermentation plant						
7	September 08	>90% pig manure from several farms containing some domestic wastewater	7.4	1.9	0.5	0.011
	September 08	fermented manure concentrate after reverse osmosis	7.3	nd ^f	0.06	0.11
	September 08	fermented manure permeate after reverse osmosis	nd ^f	nd ^f	0.0003	<0.0001
	September 08	fermented compost	nd ^f	28	0.001 ^d	0.027 ^d

^a Feed mixture containing ≈94 mg saccharin/kg dry weight. ^b pH in a 1:100 aqueous extract. ^c Referring to dry weight. Concentration in control samples from piglets fed without saccharin was <10 mg/kg. ^d mg/kg dry weight. ^e Some manure samples contain acesulfame, a marker of domestic wastewater. ^f nd: not determined.

internal standard, was from Toronto Research Chemicals, North York, Canada.

Soil Samples. Soil samples were collected in June and August 2009. Three soils were from arable land, two from fertilized meadows, and one soil was from an alpine pasture (Table 1). The sampling locations were in close proximity to those of the Swiss soil monitoring network (NABO, www.bafu.admin.ch/boden). The soils were selected to cover a wide range of properties, in particular pH, organic carbon, and texture (Table 1). Standard equipment was used for sampling soil from the top 10 cm. The soils were kept in the dark at ≈4 °C. Soil incubation experiments were set up a few days after sampling. Subsoil material for a column leaching experiment was taken from a construction site at ≈50 cm depth.

Feces, Manure, and Sewage Sludge Samples. Fresh piglet feces were collected directly in the pigsty of a farm in Switzerland. Liquid pig manure was sampled from manure pits of six farms. The grab samples were taken while stirring the manure. Details on manure composition and data on pH and dry weight are listed in Table 2. Further samples were

obtained from a manure fermentation plant. The treatment technology of this installation is addressed in the Results and Discussion section. Digested sewage sludge was obtained from four municipal WWTPs (Table 3). All these samples were kept in the dark at ≈4 °C and were processed within the next days.

Incubation of Sweeteners in Soils. Aerobic incubation experiments were carried out in Erlenmeyer flasks closed with air-permeable cellulose plugs. Portions of 2-mm sieved, field-moist soil (250 g) were filled into the flasks and fortified by dropwise addition of 1 mL of a solution containing 250 μg of acesulfame, cyclamate, saccharin, and sucralose in water/methanol (5:1). The resulting spike levels were 1 μg/g moist soil, which corresponds to inputs of ≈750 g/ha, assuming a uniform incorporation in the top 5 cm soil layer and a bulk density of 1.5 g/cm³. Spike levels were thus at the upper limit of what would result from estimated inputs (see later, Figure 1) but not high enough to induce specific degradation processes.

The soils were then thoroughly mixed and incubated at 20 °C in the dark for 63–107 d. The moisture of the soils

TABLE 3. Concentrations of Artificial Sweeteners in Digested Sewage Sludge, Canton of Zurich, Switzerland^a

WWTP	sampling date (2009)	population served	dry weight [%]	acesulfame [μg/L]	cyclamate [μg/L]	saccharin [μg/L]	sucralose [μg/L]
Gossau	November 18	12300	2.3	27	2.0	11	7.3
Regensdorf	November 03	16300	2.3	43	1.2	16	6.3
Wetzikon	November 12	27300	2.3	30	5.5	10	8.6
Zürich	November 03	410000	1.6	23	0.6	12	5.4
untreated wastewater ^b				12–43	10–65	4–18	2–9
treated wastewater ^b				14–46	<0.1–0.8	<0.1–3	2–9

^a Reported concentrations are volume-based since the hydrophilic sweeteners are primarily associated with the aqueous phase. The data may be converted to mass-based units using the dry weight provided in the Table. ^b Data from ref 2.

(22–174 g water per 100 g dry soil, corresponding to 34–60% of the maximum water holding capacity, Table 1) was regularly checked by weighing and kept constant by addition of distilled water. At appropriate time intervals, aliquots of 10 g soil were removed for extraction and analysis. Duplicate samples were taken immediately after fortification and mixing to determine the homogeneity of application, recovery, and reproducibility of extraction in the respective soils. Soil respiration was followed in three soils during 63 d, incubated in separate flasks without addition of sweeteners (12). These measurements confirmed that the soils were still biologically active after 2 months, although respiration decreased by 13–42% over time. Abiotic dissipation of the sweeteners was studied using a γ -irradiated soil (Ebikon, dose, 30 kGray, Table 1) as sterile control.

Column Leaching Experiment with Subsoil Material. A 40 × 5 cm glass column was used for this experiment. At the bottom end, the column was equipped with a glass frit and a PTFE-tubing with valve for collecting the leachate. The column was filled with 2-mm sieved soil up to a level of ≈22 cm. The soil was then saturated with groundwater from a pumping station in Zurich, not containing any detectable amounts of artificial sweeteners. The top end of the column was sealed with parafilm. Untreated wastewater from WWTP Richterswil, Switzerland was used as feed solution (24-h composite sample, collected on February 9, 2010). Portions of 50 mL wastewater were filled into PET-bottles and frozen until used. Every weekday, a portion was thawed, loaded onto the column, and allowed to freely flow through the column (1–4 mL/min). At the same time, 50 mL of leachate was collected for analysis. The wastewater portion on day 0 had not been frozen and with that, we assumed that the soil was inoculated. Freezing of the following wastewater portions guaranteed constant feed concentrations of sweeteners, organic carbon, and nutrients. The leaching experiment was conducted at 20 °C in the dark for 57 d.

Incubation of Saccharin in Pig Manure. The degradability of saccharin was investigated in manure from farm#1 (Table 2). For that, 500 mL of manure was filled into an Erlenmeyer flask and sealed with an airtight outlet valve, allowing the gas that was formed during incubation to escape. The initial concentration of saccharin in this manure sample was high enough so that additional spiking was not necessary. Manure was incubated at 20 °C in the dark for 62 d. Periodically, the flask was opened to replace evaporated water and for sampling. This experimental setup of a closed incubation vessel with periodic air contact was assumed to be representative of a closed manure pit. Since no degradation of saccharin was observed, no sterile control experiment was performed.

Extraction of Solid Samples. The hydrophilic sweeteners were extracted from soil samples with water (10 g soil with 1 L of deionized water, purified over adsorption cartridges of a Seralpur PRO90CN system from Labtec Services, Wohlen, Switzerland). After 30 min of equilibration, an aliquot was

filtered (25 mL, 0.45 μm Chromafil RC-45/25, Macherey-Nagel, Düren, Germany), fortified with internal standard (2.5 μg in 250 μL of methanol), and split into 5 portions of 5 mL for standard addition (see below). The organic-rich soil Realp (Table 1) was first suspended in 10 mL of methanol and then extracted with water. Piglet feed pellets (finely ground in a mortar) and feces were extracted in the same way but with an additional dilution step, i.e., the filtered extract was further diluted with water (1:100). Fermented compost (10 g) from a manure fermentation plant was extracted with 100 mL of water.

Extraction of Liquid Samples. Pig manure (10 g) was diluted with water (1 L). After 30 min, a small portion was filtered, further diluted depending on expected concentrations (up to 1:10), and an aliquot (25 mL) was fortified with internal standard (2.5 μg in 250 μL of methanol) and split into 5 portions for standard addition. Fermented manure and digested sewage sludge were directly filtered and analyzed with standard addition. Concentrate from the reverse osmosis treatment of fermented manure (description of the treatment technology, see Results and Discussion) was diluted with water after filtration (1:10).

LC-MS/MS Analysis. The sweeteners were analyzed with liquid chromatography-tandem mass spectrometry after online solid-phase extraction as described in ref 2. The analytical procedure, originally developed for wastewater, surface water, and groundwater, was applied to extracts from soils, feces, and manure without adaptation. Details on matrix effects, recoveries, and limits of detection are provided in the Supporting Information.

Leaching of Acesulfame and Saccharin to Groundwater: Computer Simulations. The pesticide leaching model FOCUS PELMO (version 3.3.2, available at <http://focus.jrc.ec.europa.eu/gw/index.html>), developed for pesticide registration in Europe, was used to simulate degradation and vertical transport of acesulfame and saccharin in soils. Simulations were performed for four European standard climate and soil scenarios (Châteaudun, France; Hamburg, Germany; Okehampton, UK; and Piacenza, Italy). Generally, this model is designed to yield realistic worst-case concentrations in soil leachate (at 1 m depth) as the scenarios represent vulnerable environmental conditions. Actual concentrations in groundwater are expected to be lower, also due to further dilution of soil leachate.

In a first set of simulations, it was assumed that acesulfame ends up in soils via irrigation with wastewater-loaded surface water (see Results and Discussion). For that, the crop maize was selected, combined with the scenarios Châteaudun or Piacenza (both run with irrigation activated). Annual inputs of 100 g acesulfame/ha were assumed to occur in four discrete “irrigation events” on May 1, June 1, July 1, and August 1, over a period of 20 years. A half-life (time to 50% dissipation, DT₅₀) of 6.1 d was used for acesulfame (geometric mean of normalized data, Table 1) with the standard temperature and moisture correction of the program. A K_{oc} value for acesulfame was not found in the literature. Simulations were

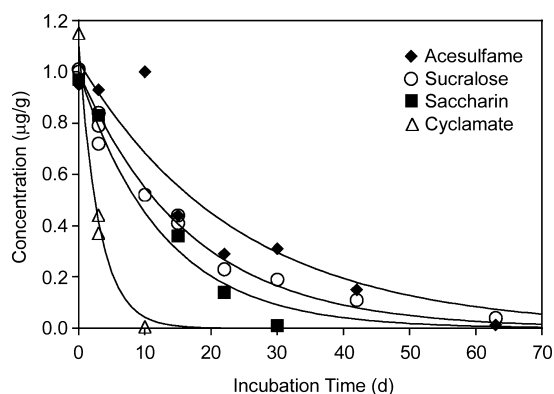


FIGURE 2. Degradation of artificial sweeteners in soil (ns (Table 1). Lines show fits according to a first-order kinetic model.

thus run with the K_{oc} for saccharin because of its structural similarity (see below).

In a second set of simulations with winter cereals and the scenarios Hamburg, Okehampton, or Piacenza, it was assumed that saccharin is applied to soils associated with pig manure in amounts of 500 g/ha on March 1 and August 1 (see Results and Discussion). A DT_{50} of 3.3 d was used for saccharin (Table 1). A mean K_{oc} of 8.9 mL/g was taken from the review reports and risk assessments of the European Union on the herbicides metsulfuron-methyl, tribenuron-methyl, and propoxycarbazone, all having saccharin as a common soil metabolite (available at http://ec.europa.eu/sanco_pesticides). In these reports, good correlation was found between soil–water distribution coefficients and organic carbon content of the soils, and K_{oc} values are thus representative of the sorption behavior of saccharin in soils. The pH values of the soils used in the sorption studies ranged from 5.7 to 8.1, i.e., these K_{oc} values refer to the anionic form of saccharin ($pK_a \approx 1.5$).

Results and Discussion

Degradation of Sweeteners in Soils. The biodegradability of artificial sweeteners was studied in six soils under aerobic conditions (Table 1). Within two months of incubation, the four compounds were degraded to residual amounts of less than 10%, except for acesulfame in soil Zuzwil ($\approx 60\%$ degradation) and sucralose in soil Realp ($\approx 30\%$ degradation after 63 d and $\approx 50\%$ after 107 d). A first-order kinetic model fitted the concentration data reasonably well (software aquasim, www.aquasim.eawag.ch; one example is shown in Figure 2). Half-lives (DT_{50}) of the sweeteners are listed in Table 1. Mean, moisture corrected DT_{50} values were 0.8, 3.3, 6.1, and 9.0 d for cyclamate, saccharin, acesulfame, and sucralose, respectively. Degradation of sucralose tended to be slower at low pH, whereas for the sulfoamide sweeteners, no obvious pH dependence was observed. No correlation was found between DT_{50} values and organic carbon content or texture of the soils.

The fast degradation of cyclamate and saccharin in soils is consistent with the extensive elimination observed in WWTPs (≈ 99 and $\approx 90\%$, respectively 2, 4). For acesulfame and sucralose, however, fairly rapid degradation in soils is in contrast to their persistence in WWTPs. This may be rationalized by the presence of different microbial communities in activated sludge and soil. In particular, yeasts and other fungi are more prevalent in soils than in activated sludge (13). However, this does not necessarily imply that fungi are responsible for degradation of these sweeteners in soils. Furthermore, residence times in activated sludge basins of typically a few hours are obviously much shorter than contact times in soils. Such differences in elimination

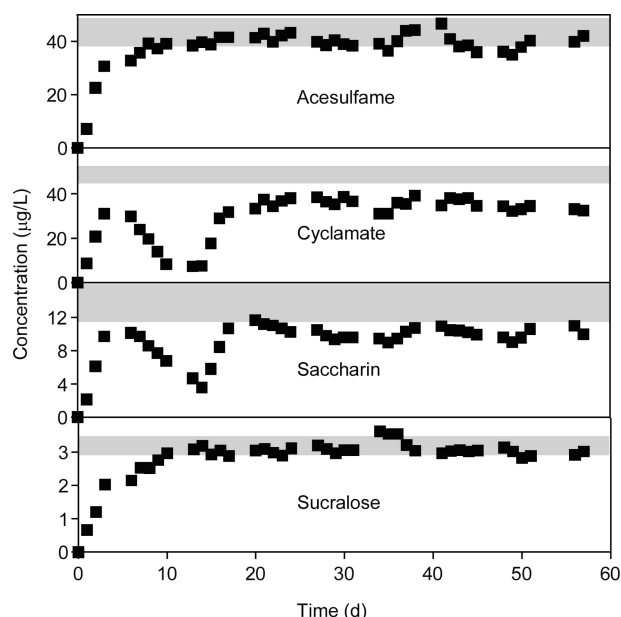


FIGURE 3. Concentrations of artificial sweeteners in the leachate of a subsoil column percolated with untreated domestic wastewater during 57 d. The gray bars indicate ranges of concentrations measured in the feed solution.

behavior have also been observed for other chemicals. For example, the fungicide propiconazole is not transformed in WWTPs (14), whereas in soils, the compound is degraded with DT_{50} values of 29–70 d under laboratory conditions (available at http://ec.europa.eu/sanco_pesticides).

In earlier studies on sucralose in soils (15, 16), 50% mineralization was observed within ≈ 1 –3 months of aerobic incubation, which is in line with our findings. Degradation of sweeteners in soils appears to be biologically mediated, since in a sterile control experiment, no (acesulfame, saccharin, and sucralose) or a considerably slower (cyclamate) dissipation was observed (Table 1).

Degradation of Sweeteners in Subsoil Fed with Untreated Wastewater. Biodegradation rates usually decrease with soil depth due to decreasing biological activity in subsoils. This may be different in a situation where untreated domestic wastewater seeps into a subsoil through a leaky sewer over extended periods of time (Figure 1). The degradability of artificial sweeteners was therefore investigated in a column leaching experiment, where untreated wastewater was percolated through subsoil material over a period of 57 d. Concentrations were determined in the leachate of this column and compared with those in the feed solution. During the first days, concentrations of the four sweeteners in the leachate increased continuously and with similar rates relative to the feed concentrations (Figure 3). Retardation was minimal in the subsoil, which is reasonable since sorption of the hydrophilic compounds to the sandy material with only 0.5% organic carbon was expected to be weak.

In the second week, concentrations of cyclamate and saccharin decreased again to levels of ≈ 16 and 27% of the feed concentrations, respectively, probably due to growth of microorganisms capable of degrading these compounds within a few days. In contrast, concentrations of acesulfame and sucralose did not decrease and reached those in the feed solution, indicating that the two sweeteners were quite stable in this environment.

In the third week, concentrations of cyclamate and saccharin once more increased to $\approx 76\%$ of the feed concentrations. We assume that environmental conditions in the subsoil had changed, in particular, the redox potential must have decreased (precipitation of iron(hydr)oxides was

observed in the eluate). Degradation of cyclamate and saccharin thus seems to be less favorable under these altered conditions.

Extrapolation of this laboratory experiment to a real situation where wastewater seeps through a leak in a sewer into a subsoil is, of course, difficult and should not be done in a quantitative sense. However, the data suggest that cyclamate and saccharin are degradable in such an environment and that the redox potential has a pronounced influence on the degradation rates. Acesulfame and sucralose, on the other hand, seem to be fairly stable.

In another study, artificial sweeteners were analyzed in wells nearby a soil aquifer treatment site where secondary effluent from a WWTP was spread in percolation basins (4). Cyclamate and saccharin were found at levels up to 400 ng/L in WWTP effluent but only in traces in the observation wells. Measured concentrations of acesulfame and sucralose in the wells, however, indicated that they were quite stable under these environmental conditions (residence times from percolation basins to the wells were 1.5 months to >1.5 years).

Furthermore, degradation of artificial sweeteners was studied in a fixed-bed bioreactor, where aerated surface water was pumped in recirculation over a column filled with sintered glass beads (6). In this experiment, simulating aerobic river bank filtration, complete removal of cyclamate and saccharin was observed within 15 and 20 d, respectively, whereas acesulfame and sucralose were not eliminated during 92 d.

Saccharin in Piglet Feces. In the EU and in Switzerland, saccharin is registered as feed additive for piglets up to an age of 4 months with a maximum content of 150 mg/kg feedingstuff (http://ec.europa.eu/food/food/animalnutrition/feedadditives/index_en.htm). The sweetener is supposed to facilitate the adaptation to dry feed after the suckling period. For this study, a group of 20 piglets was fed with a standard cereal mixture to which saccharin had been added (≈ 94 mg/kg dry feed pellets).

Feces from 6–9 week old piglets, collected 1–4 weeks after continuous feeding with saccharin, contained the sweetener at concentrations of 240–260 mg/kg dry weight (Table 2). Considering that a pig excretes 0.20–0.25 kg feces per kg feed (dry weight basis, personal communication, P. Stoll, Agroscope), the data suggest that saccharin was largely excreted. High excretion rates have previously been reported for other animals and humans (17). The sweetener was not found in feces from control piglets fed without saccharin (<10 mg/kg).

Saccharin in Liquid Pig Manure. In the study area, feces and urine in the pigsties are typically flushed with water resulting in rather liquid manure, which is usually stored in manure pits and often mixed with manure from other farm animals. The occurrence of saccharin was investigated in various “real-life” manure samples from pig farms in Switzerland (Table 2). The sweetener was detected in all samples at concentrations ranging from 0.3 to 12 mg/L (Table 2). Piglet manure that was mixed with manure from other farm animals, rainwater, or domestic wastewater tended to show lower concentrations than manure originating primarily from piglets fed with saccharin-containing food. The presence of domestic wastewater in manure #4 and #7 was confirmed by detection of acesulfame which is not registered for animal feed (0.048 and 0.011 mg/L, respectively).

The fact that saccharin occurred at fairly high concentrations in a number of manure samples stored for different periods of time suggested that the compound is quite stable in manure. Moreover, stability of saccharin was confirmed in a batch incubation experiment. In pig manure from farm #1, no degradation was observed within 62 d of storage at 20 °C. It can thus be expected that saccharin ends up in soils in

considerable quantities with the application of pig manure (Figure 1, discussion, see later).

Fate of Saccharin and Acesulfame in a Manure Fermentation Plant. In certain areas of Switzerland, livestock density is quite high, potentially leading to excessive nutrient loading of farmland and, consequently, eutrophication/pollution of surface and groundwater. The amount of manure per hectare that may be applied as fertilizer is therefore subject to legal restrictions. Many farmers thus have agreements and provide manure to crop farmers. An alternative utilization practice is the fermentation of manure for biogas production.

In Switzerland, a first large-scale manure fermentation plant was recently put into operation (www.sfpinwil.ch). This installation processes liquid manure from ≈ 70 farms, predominantly pig manure (maximum capacity, $\approx 45'000$ m³ per year). Manure is continuously introduced into fermentation tanks operating at 35–40 °C. The fermentation process generates biogas equivalent to ≈ 18 GWh. After a mean residence time of ≈ 20 d, the solids are separated, dewatered, and further composted, yielding a phosphorus-rich fertilizer (≈ 1000 t/a). The liquid fraction of the fermented manure undergoes an ultrafiltration and reverse osmosis step yielding an ammonium-rich concentrate (≈ 7700 m³/a) and a permeate ($\approx 30'000$ m³/a) that is further treated in the municipal WWTP.

Saccharin was detected in all samples taken from this installation at concentrations of 0.5 mg/L in raw liquid manure but only 0.06 mg/L in the manure concentrate, 0.0003 mg/L in the permeate, and 0.001 mg/kg in compost (#7 in Table 2). Saccharin was thus degraded by more than 95% in the fermentation process.

Furthermore, the sweetener acesulfame was found in these samples, indicating the presence of domestic wastewater (Table 2). Raw manure contained 0.011 mg/L acesulfame, whereas the concentration in the manure concentrate (0.11 mg/L) was 10× higher. Considering an enrichment factor of ≈ 6 from raw manure to final concentrate and assuming that the grab samples were more or less representative, this indicates that acesulfame is stable in the fermentation process.

Sweeteners in Digested Sewage Sludge. The sweeteners were also analyzed in four sewage sludge samples from digestion tanks of municipal WWTPs (Table 3). The compounds were detected at concentrations of 23–43 μ g/L acesulfame, 1–6 μ g/L cyclamate, 10–16 μ g/L saccharin, and 5–9 μ g/L sucralose. These concentrations are similar to those previously found in untreated domestic wastewater, except for cyclamate (Table 3).

In these WWTPs, raw sewage sludge is separated in the primary clarifiers and is a mixture of primary sludge and excess activated sludge from the secondary clarifiers. The water phase of the raw sewage sludge is thus basically identical to that of untreated wastewater, and for the hydrophilic sweeteners, which are primarily associated with the aqueous phase, similar concentrations can be expected. However, the compounds may then be degraded in the digestion tanks, where the sludge typically remains ≈ 20 d under anaerobic conditions. This obviously is the case for cyclamate for which an elimination of $\approx 90\%$ was observed (Table 3), whereas the other three sweeteners seem to be quite stable. The apparent stability of saccharin in sewage sludge digestion tanks is in contrast to its efficient removal in the manure fermentation tanks (see above).

Comparison of Entry Pathways of Sweeteners to Soils. In the following, we compare and quantify possible inputs of artificial sweeteners to soils (Figure 1). Inputs via *irrigation* of agricultural fields depend on origin/composition and quantity of irrigation water. Assuming a worst-case situation that treated wastewater (typical concentrations, see Table 3)

is used for an annual irrigation corresponding to 300 mm of precipitation (equivalent to 3000 m³ per hectare), sweeteners may get into soils in amounts of 40–140 g acesulfame/ha, <3 g cyclamate/ha, <10 g saccharin/ha, and 6–30 g sucralose/ha.

Artificial sweeteners were found at µg/L concentrations in *digested sewage sludge* (Table 3), which may be utilized as fertilizer in certain countries. However, with 1–2 applications of ≈40 m³ sewage sludge per hectare and season, only small amounts of 0.5–4 g/ha may end up in agricultural soils.

Liquid pig manure may be a further source of saccharin in soils. With 1–2 applications of ≈40 m³ pig manure per hectare and season (concentrations, 0.3–12 mg/L, Table 2), loadings of saccharin would amount to 20–1000 g/ha. Moreover, saccharin is a soil metabolite of several *sulfonylurea herbicides*. Considering typical application rates of 5–50 g/ha in cereals and metabolite formation fractions of <10–50% (http://ec.europa.eu/food/plant/protection/evaluation/database_act_subs_en.htm), up to 25 g saccharin/ha may be formed in soils after herbicide application.

Due to *leaks in sewers*, untreated domestic wastewater (typical concentrations, see Table 3) may seep into subsoils. Assuming an average exfiltration rate of 1% (18, 19) in a densely populated area with, for example, 4000 inhabitants per km², and a per-capita wastewater discharge of 0.5 m³/d, annual amounts of <1–5 g/ha may be lost via this pathway. On a larger scale, leaks in sewers will thus not contribute significantly to environmental loading with sweeteners. Locally, however, exfiltration rates may be higher.

Finally, wastewater from *septic tanks* may be discharged in leaching fields. In Europe, septic systems are generally limited to remote areas and were therefore not further considered in this study. However, in areas where septic systems are widespread, inputs from such systems to soils and further to groundwater may be significant.

This overview illustrates that, in general, loadings of artificial sweeteners to soils are low, in the order of a few grams per hectare and year (Figure 1). Higher inputs of acesulfame may be expected in situations where considerable amounts of wastewater-polluted surface water are used for irrigation. For saccharin, pig manure is by far the main source for soil loading in areas where it is used as feed additive. Therefore, in the last section, the risk of leaching of acesulfame and saccharin from soils to groundwater will be evaluated for these two situations with computer simulations.

Leaching Potential of Sweeteners from Soils to Groundwater. The pesticide leaching model FOCUS PELMO, developed for pesticide registration in Europe, was used to simulate degradation and vertical transport of acesulfame and saccharin in soils.

For acesulfame applied with irrigation water, it was assumed that maize fields are irrigated with the equivalent of 300 mm treated wastewater corresponding to an annual load of 100 g acesulfame/ha. Predicted peak concentrations in the soil leachate at 1 m depth are ≤0.06 and ≤0.002 µg/L for the scenarios Piacenza and Châteaudun, respectively, whereas annual mean concentrations are 0.009 and <0.001 µg/L, respectively (80% percentile of annual mean concentrations, further details on parameters and assumptions, see the Experimental Section). These low concentrations may in part be due to the fact that, during dry periods, evapotranspiration is expected to be relatively high so that downward vertical transport of water in soils is limited. Moreover, degradation rates will be higher at elevated temperatures. Considering that this modeling represents worst-case conditions with respect to leaching, irrigation is thus not expected to contribute significantly to the observed high acesulfame concentrations in groundwater. In fact, concentrations up to 5 µg/L were shown to result from known, substantial

infiltration of wastewater-polluted surface water through stream beds (2).

For saccharin applied to soils associated with manure in annual amounts of 1000 g/ha, computer simulations predict peak concentrations in soil leachate of up to 1.3, 0.2, and 1.7 µg/L for the scenarios Hamburg, Okehampton, and Piacenza, respectively (crop, winter cereals; details, see the Experimental Section), and mean concentrations of 0.02, 0.02, and 0.3 µg/L, respectively.

Indeed, saccharin was detected in groundwater from a pumping station in Switzerland at concentrations up to 0.26 µg/L. Several points suggest that saccharin may have reached groundwater at this pumping station after application of pig manure: (i) the wastewater marker acesulfame was not detected in these samples, which indicates little if any infiltration of polluted surface water. (ii) The pumping station was located in a rural area with little discharge of wastewater but intensive agriculture. (iii) High nitrate concentrations were measured in groundwater. (iv) Samples were taken in autumn, when leaching of many compounds is more likely than during spring and summer (due to less evapotranspiration and lower temperatures). Under certain conditions, the presence of saccharin in groundwater samples may thus indicate application of pig manure on farmland and leaching to groundwater.

Acknowledgments

We thank Y. Aeby (Agroscope Posieux, Switzerland) and numerous farmers for samples of pig feces and manure, C. Eggerschwiler (SwissFarmerPower, Inwil, Switzerland) for samples from the manure fermentation plant, M. Koch and E. Gansner (AWEL, Office for Waste, Water, Energy, and Air of the Canton of Zurich, Switzerland) for sewage sludge samples, and H. R. Oberholzer, A. Bonvicini, R. Flisch, and R. Meuli (Agroscope Reckenholz, Zurich) for the determination of soil parameters. This study was financed by the Federal Office for the Environment (Bern, Switzerland, B. Hitzfeld, R. Kozel, A. Weber) and by AWEL (M. Koch).

Supporting Information Available

Details on the analytical method (matrix effects, recoveries, and limits of detection). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES1031272