

In situ impacts of a flooding event on contaminant deposition and fate in a riparian ecosystem

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Abstract

Purpose Floodwaters contain a mixture of organic contaminants which affect both the water and soil quality within flooded regions. This study is the first to describe the chemical behavior of organic contaminants mobilized during the 2010 flooding event of the Rio Grande. The study compares two sites: one directly impacted by outfall from municipal sources and one primarily impacted by rural runoff.

Materials and methods This study characterized the in situ cycling of organic contaminants (triclosan, ciprofloxacin, and atrazine), their depositional mechanisms, and the post-flood dynamics within riparian soils over 6 months. Water quality (pH, salinity, alkalinity, turbidity, N, and P) of the Rio Grande at four sites within Webb County, TX, was monitored for 3 months pre-flooding and 6 months post-flooding in order to determine contaminant levels along the Webb County border. Soil physicochemical properties (pH, CEC, and EC) were assessed for 6 months at two sites post-flooding: within the municipal area of both Laredo, TX, USA, and Nuevo Laredo, Mexico (LCC site), and upstream of the site near the edge of Laredo, TX (MR site).

Results and discussion Low levels of contaminants were detected in the watershed year-round with levels increasing during the flood. Floodwaters had a lower pH than nonflooding

conditions, resulting in greater partitioning of both triclosan and ciprofloxacin to particles within the water column with no change detected in atrazine behavior. Soil samples (0–2-cm depth) showed an increase in clay-sized particles (up to 6–14 %) and contaminant concentrations similar to that of water column particles. Organic contaminants were uniform in concentration throughout the soil profile (2–30 cm), demonstrating the impact of infiltration. Both triclosan and atrazine decayed away at rates of 23 ± 2 and 16 ± 1 days, respectively, with no decay of ciprofloxacin detected. Vertical mobility of contaminants within soils was not detected.

Conclusions This study was able to distinguish the influx of contamination contributed by particle deposition from that due to infiltration of the contaminated floodwaters. Further, our data indicates that outfall/effluent contaminants, such as ciprofloxacin, may persist in riparian soils post-flooding. Agricultural management should consider potential exposure and accumulation of floodwater contaminants in crops.

Keywords Contaminant cycling · Contaminant transport · Flood contamination · Endocrine disruptors · PPCPs

1 Introduction

Flooding of agricultural, industrial, mining, shipping, and municipal areas allows for the mobilization of a suite of organic contaminants in mobilized sediments and runoff. As floodwaters recede, contaminants are deposited in soils adjacent to streams and rivers. The behavior of these compounds in floodwaters and soils, to which they are transported, still needs to be better defined. Both water and soils are dynamic media requiring that sampling be performed immediately in order to properly model contaminant dynamics and retention within the system during periods of flooding.

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Between the years of 1999 and 2002, pharmaceutical sales increased by over 25 % worldwide with 51 % of the total sales occurring in the USA by 2002 (Xia et al. 2005). These compounds are continuously released into the environment due to human consumption and pose a potentially significant threat to the integrity of aquatic ecosystems (Barnes et al. 2008; Focazio et al. 2008). Triclosan, a chemical of emerging concern, is one of the most widely used broad spectrum antimicrobials found in detergents, personal hygiene products, plastics, and textiles (Daughton and Ternes 1999; USEPA 2009), and it is one of the most prevalent PPCPs found in freshwater systems (Kolpin et al. 2002). Both triclosan and ciprofloxacin have the potential to be transported to soils through floodwaters and/or sewage sludge applications possibly affecting non-target species and increasing bacterial resistance (Halling-Sørensen et al. 1998, 2003; Wilson et al. 2003; Hinthner et al. 2011; Svenningsen et al. 2011; Drury et al. 2013). There has also been a tenfold increase in pesticide use in the USA from 1945 to 2000 despite concerns of environmental damage they may cause (Pimentel 2009). Atrazine application rates range between 70 and 80 million pounds per year based on surveys conducted from 1992 to 2007 (Thelin and Stone 2010). The pressure for continued development of new compounds for both PPCPs and agricultural use poses difficulties for management in regard to the options available to alleviate concerns regarding these compounds entering aquatic ecosystems. Once present in the watershed, contaminants are mobilized and transported in floodwaters potentially impacting floodplains hundreds of miles from the initial contamination point.

It is commonly accepted that the pH of a water body is the primary factor in determining partitioning behavior of an organic compound, thereby determining if the compound will remain aqueous or adsorbed to particles (Hari et al. 2005; Robberson et al. 2006). Additional alterations of organic contaminants in the water column may also be due to hydrolysis and photolytic processes (Wilson et al. 2009; Kummerer 2009).

Modeling of contaminant depositional patterns within riverine systems is primarily based on hydraulic and geospatial techniques, with the efficiency of these models dependent on post-depositional field data (Stewart et al. 1998; Schultz et al. 2009). During flood events, sediments and riparian soils serve as a repository for a number of particulate bound contaminants in riverine and estuarine systems, and therefore serve as a major source of contaminant mobilization (Pizzuto 1987; Cooper et al. 2003; Forstner et al. 2004; Schwartz et al. 2006; Hilscherova et al. 2007). Continued monitoring of historically contaminated areas has shown that the distribution of organic contaminants within recovering systems is a complicated fluctuation between storage and redistribution of materials based on flow regime (Pizzuto 1987; Cantwell et al. 2010; Micić et al. 2013). One of the primary concerns in modeling is the quantification of particle deposition based

on hydrological flow models used to identify areas receiving disproportionate quantities of contaminated particulate matter (Stewart et al. 1998). Sediment modeling demonstrates that changes in water column parameters and boundary conditions are significant factors in contaminant dynamics (Schultz et al. 2009).

Evidence of contaminant mobilization and deposition associated with flooding has also been shown in post-flood studies of floodplain soils and associated organisms. Sampling of sediments redeposited in areas with low turbulence, typical of floodplains and stream banks, has shown that elevated levels of contamination in flooded areas are due to a redistribution of contaminants within the watershed (Hamers et al. 2006; Cobb et al. 2006; Hilscherova et al. 2007). Flooding of agricultural lands mobilizes herbicides within floodwaters, increasing herbicide concentrations within floodplain soils downstream of the application site due to the deposition of particle-adsorbed herbicides (Chong et al. 1998). A change in plant growth has also been associated with an influx of contaminated particles due to flooding (Kooistra et al. 2004). Lastly, soil invertebrates have demonstrated bioaccumulation of contaminants in post-Hurricane Katrina flooded soils (Harmon and Wyatt 2008).

In terrestrial systems, it has been determined that the absorption of a number of compounds in soils is correlated to the combined effect of the cation exchange capacity (CEC), electrical conductivity (EC), and pH of a system. Other studies have indicated that triclosan readily decays in soils with neutral to alkaline pH and high organic content (Al-Rajab et al. 2009; Xu et al. 2009). Ciprofloxacin's mobility and bioavailability is primarily dependent on CEC, and it appears to be persistent in soils (Golet et al. 2003; Vasudevan et al. 2009). Atrazine has also been documented as a persistent soil contaminant with low levels of percolation; the primary driving force in the removal of atrazine is biodegradation (Lupi et al. 1988). Few studies have demonstrated that there is an interaction between the anionic exchange in aqueous systems as well (Robberson et al. 2006).

This research was performed during the flooding of the Rio Grande which began on July 5, 2010, due to a combination of tropical storms and water releases from Amistad Reservoir. The flood peaked on July 8, 2010, at 42 ft above the river base level. This was the second largest flood in 60 years; the largest flood occurred in 1954, peaking at 62 ft. Since then, the reservoir system has been developed for water storage and flood control of the region. However, excessive rainfall caused by Hurricane Alex overflowed the storage capacity of Amistad Reservoir, resulting in mass releases to protect the dam and to limit damage downstream. Controlled releases of water (>4000 m³/s) from Amistad Reservoir resulted in flow levels exceeding flood controls for the lands between the Amistad and Falcon Reservoirs, approximately 250 mi. of river (Montero 2010).

The Rio Grande outside of Laredo, TX, has been regularly monitored for contaminant levels prior to the flood event. The monitoring program allowed us to assess the differences in chemical concentrations and behavior within the Rio Grande during both flooding and typical flow conditions. Flooding can alter a number of parameters that may influence the distribution of contaminants within the watershed, most importantly particulate mobilization/redistribution and shifts in the pH of the water column, potentially altering the partitioning of compounds. Secondly, having the water column data from the flood itself allowed us to better assess the mechanisms distributing the contaminants within the floodplain soils. Lastly, this project assesses, within the root zone, the impact and retention of organic contaminants potentially available to plants over a period of 6 months. This data can be used in flood-prone regions to assist management organizations and property owners in identifying areas in which contamination may be most severe.

2 Materials and methods

2.1 Water sampling

Water sampling sites were monitored monthly for general water quality and contaminant levels beginning 3 months prior to the flood through the 6 month period of post-flood analysis. Due to the availability of bridges and structural access to the river, monitoring was also conducted during peak flood conditions. Samples were collected from four sites within the Laredo, TX, city limits: (1) at Rio Bravo-Laredo city limits; (2) at the International Bridge II; (3) the Jefferson Water Treatment Plant (at the intake for the drinking water plant); and (4) McNaboe Park. Two of these sites, the International Bridge II and Del Rio Park, are adjacent to the field sampling sites used for this research (see below). The Rio Bravo-Laredo city limits were selected as a representative site to determine the cumulative contamination released into the river from both Laredo, TX, and Nuevo Laredo, Mexico. Del Rio Park was selected as the point furthest upstream in the city to determine the contamination levels flowing into the city limits. These sites were originally selected due to accessibility to the river and because they are areas of concern for contamination even during low-flow conditions.

In situ data were collected using a YSI 6600 V2 multiple probe sondes (with interchangeable ROX sensors for dissolved oxygen, pH, salinity, alkalinity, turbidity, fluorescence, and temperature) and recorded with a YSI 650MDS data logger. Flow rates were collected from the in situ gauges monitored by the International Boundary Water Commission (IBWC) and the Texas Commission on Environmental Quality Control (TCEQ) via flow gauges at Columbia Bridge, International Bridge II and Del Rio. Water samples were placed

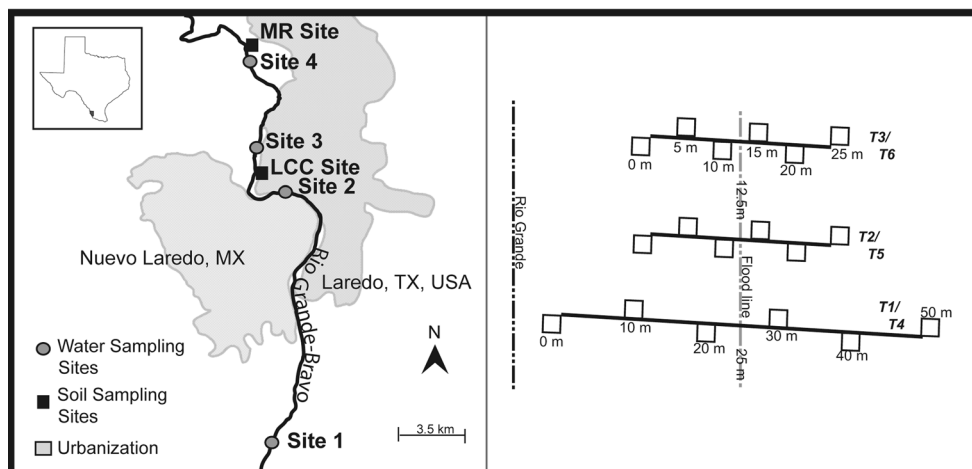
into HDPE amber bottles, filtered, acidified with H_2SO_4 and stored at 4 °C for further analysis. Each 1 l sample was filtered through 0.2 μm filters to collect the suspended matter for contaminant extractions and to determine the total suspended matter of the water column. The total suspended matter was further used to determine the concentration of contaminants adsorbed to the suspended particulates within the water column and to determine partitioning coefficients for the contaminants.

2.2 Soil sampling and physicochemical analysis

For the purposes of this study, two sites were selected for sampling based on proximity to the river with similar plant diversity/type and protection from industrial/agricultural processes. The two sites were as follows: (1) the Lamar Bruni Vergara Environmental Science Center Nature Walk maintained by the Laredo Community College (LCC Site) near downtown Laredo, TX, and (2) undeveloped lands near Mines Road used by US Border Patrol for monitoring the river (MR site) at the northern (upstream) edge of the city. Both sites were dominated by buffelgrass, *Pennisetum ciliare* (L.), and sparsely populated with common native woody species, making them ideal for sampling and retaining transects with visible flags. The MR sampling site contained a cryptobiotic crust present in both flooded and nonflooded areas which was not present at the LCC sampling site. Thus, the microbial community may differ between the two sampling areas.

Immediately after floodwaters had receded, transects were delineated at the two sites and initial samples were collected on July 16, 2010. Samples were collected immediately in order to document initial conditions prior to any environmental and biological alterations of the soils (such as rain events or animal disturbance) and to minimize the effects of microbial activity within the rhizosphere. Additional samples were collected from these transects at 6, 14, and 24 weeks following the flood. Transects were laid out perpendicular to the topography (to the maximum slope) at each site, geo-referenced and marked for ongoing sampling. Each transect was positioned to span an equal distance into both the flooded and nonflooded areas with the flood line denoted by the fine layer of silt on both the plants and soils. Three transects were delineated at each of the sites with alternate 1-m² quadrats sampled at every point: a 50-m transect with sampling points at every 10 m and two 25-m transects with sampling points at every 5 m (Fig. 1). Soil within each quadrat were sampled at five equidistant points and consolidated for each quadrat. The dominant plant in both sampling areas was buffelgrass that had a shallow rhizosphere of <10 cm in all locations. Our initial intent was to sample at the surface (0–2 cm) and at a depth of at least twice that of the root zone (10 cm, 2–20 cm) to assess the chemical availability to plants, and eventually determine if the organics were retained within this zone. After the initial

Fig. 1 Map of study area including the sampling sites (water: sites 1 to 4; soil: LCC and MR sites) with areas of urbanization designated and a schematic diagram of transects



sampling, we extended this depth down to 30 cm (collected at 20–30 cm) to further assess the penetration and mobility of these compounds within the flood plain, post-deposition. At the initial sampling (0 weeks), 36 samples were collected from each site (18 quadrats at two depths per sampling site); 54 samples were then collected at every subsequent sampling time (18 quadrats with three depths each per sampling site) at 6, 14, and 24 weeks post-flooding. Number of samples increased due to the addition of a third depth (20–30 cm) to the sampling regime. The initial samples were recoded so that each position and depth had the appropriate sample number for statistical comparisons.

Samples were collected using a 1" diameter nickel-plated soil probe to a depth of 20 cm in July 2010 and down to 30 cm for the remaining sampling periods. Samples were then segmented by horizon: the upper (0–2 cm, surface/particle deposition), root zone (2–20 cm), and deep soils (20–30 cm, below the root zone). All samples were collected into airtight zip-top bags and stored on ice for transport. From these samples, 25 g were partitioned and immediately dried at 50 °C (to a constant mass) for organic contaminant analysis. Soil moisture was determined from these samples. The remaining soil samples were then air-dried in paper bags for 7 days, then sieved with a 2-mm mesh screen prior to organic carbon/nitrogen, pH, EC, CEC, available phosphate, and soil texture analysis.

Soil pH and EC were determined using a 2:1 ratio of de-ionized water to air-dried, sieved soils (*v/w*) that were shaken and centrifuged. The resulting supernatant was then analyzed using a VWR Symphony SB80PC pH/conductivity meter. CEC was analyzed using the sodium acetate method as described by Chapman (1965). Available phosphorous was extracted using the Olsen method (Pierzynski 2000). Soil texture was determined using the hydrometer method by Gee and Bauder (1982). Total organic carbon and total nitrogen were evaluated using combustion methods modified (with increased acidification) from Wallace et al. (2004).

Changes in soil pH, EC, and contaminant concentrations over time were further examined by a repeated measures ANOVA to determine the effect of time, flooding, and depth along with the interactions between factors. Since the 20–30-cm depth was missing from the first sampling time (week 0), a PROC MIXED was used followed by a Tukey's post hoc test to determine differences between samples. For soil pH and EC, only transects 1 (LCC site) and 4 (MR site) were used in this analysis since these were the longest transects (50 m). For each depth, the overall main effects of flooding and time were examined further using a repeated measures ANOVA along with a MANOVA to determine the effects of these factors over time. Where flooding was significant, this analysis was followed by a one-way ANOVA and Tukey's HSD post hoc test to determine differences between quadrats based on location relative to the river for each sampling time (see the Tables in the Electronic Supplementary Material for complete data). For the contaminant analysis, all six transects were evaluated to determine differences between quadrats based on relative distances from the river. Statistics were performed using SAS version 9.3 software (SAS Inc., Cary, NC) for the repeated measures ANOVA analysis.

2.3 Contaminant analysis

Procedures for extracting triclosan from both water and soil/suspended particulate samples were originally described by Wilson et al. (2009). Water column samples (1 l) were filtered through 15-cm Whatman GF/F filters via N₂ pressure filtration (<15 psi). Samples were spiked with 10 ng (per liter water) of ¹³C-labeled triclosan (Cambridge Isotopes, MA) as a recovery standard. Water was extracted using dichloromethane (DCM) separations with a sep-funnel (DCM; 10 ml/250 ml of sample four times, then repeated until a full liter was extracted). Samples were then concentrated and passed through sodium sulfate and solid phase extraction disks (Oasis silica disks), eluted with ethyl acetate, and then concentrated

to 1 ml prior to derivatization. Suspended particulate and soil samples were dried at 50 °C (to a constant mass), hand ground, and spiked with 25 ng of ¹³C-labeled triclosan (Cambridge Isotopes, MA) as a recovery standard. For extractions, 50–250 mg of particulate was used, depending on the amount available, or 2 g of dry soil was utilized. Solid-phase extractions were performed using sonication in a 1:1 mixture by volume of acetone and methanol at 25 °C (15 min, three times). Samples were concentrated and passed through sodium sulfate and solid-phase extraction disks (Oasis silica disks), eluted with methanol, and then concentrated to 1 ml prior to derivatization. Aliquots (200 µl) from all extracts were dried under N₂ gas and then derivatized with MTBSTFA followed by resuspension in 200 µl of ethyl acetate. Samples were then analyzed using gas chromatography–mass spectrometry (GC-MS) operating in electron impact select ion monitoring (ELI-Sim) mode.

Procedures for extracting ciprofloxacin from water were modified from Golet et al. (2001) and Lee et al. (2007). Water column samples (1 l) were spiked with 10 ng of ¹³C-labeled ciprofloxacin (Cambridge Isotopes, MA) as a recovery standard. Samples of the acidified and filtered water samples were extracted using 30-µm Oasis WCX-SPE cartridges (mixed-phase cation-exchange) pretreated with methanol. Disks were washed with acidified water (pH ≤3) then eluted with a mixture (v/v) of 20:75:5 methanol/acetonitrile/formic acid. Suspended particulate and soil extraction procedures for ciprofloxacin were modified from Golet et al. (2001) and Pico and Andreu (2007). Suspended particulate and soil samples were dried at 50 °C (to a constant mass), hand ground, and spiked with 25 ng of ¹³C-labeled ciprofloxacin, as a recovery standard. For extractions, 50–250 mg of particulate was used, depending on the amount available, and 2 g of dry soil was utilized. Solid-phase extractions were performed using sonication in a 1:1 mixture by volume of aqueous phosphoric acid (pH=2) and acetonitrile at 100 °C. The extract was then filtered using 30-µm Oasis WCX SPE cartridges pretreated with methanol; disks were washed with acidified water (pH ≤3) and then eluted with a mixture (v/v) of 20:75:5 methanol/acetonitrile/formic acid. Aliquots (200 µl) from all extracts were dried under N₂ gas then derivatized with MTBSTFA, followed by resuspension in 200 µl of ethyl acetate and analyzed using GC-MS operating in ELI-Sim mode.

The procedure for extracting atrazine from water samples was originally described by Eisenreich et al. (1994). Water column samples (1 l) were filtered through 15-cm Whatman GF/F filters via N₂ pressure filtration (<15 psi). Samples were then spiked with 10 ng (per liter water) of ¹³C-labeled atrazine (Cambridge Isotopes, MA) as a recovery standard. Water samples were extracted using solid-phase extraction disks (Oasis silica disks) with 7 ml of 85 % dichloromethane (DCM) and 15 % methanol (MeOH) solution, by volume. Suspended particulate and soil samples were dried at 50 °C

(to a constant mass), hand ground, and spiked with 25 ng of ¹³C-labeled atrazine (Cambridge Isotopes, MA), as a recovery standard. For extractions, 50–250 mg of particulate was used, depending on the amount available, or 2 g of dry soil was utilized. Solid-phase extractions were performed using sonication in a 1:1 mixture, by volume, of acetone and methanol at 25 °C (15 min, three times). Samples were concentrated and passed through sodium sulfate and solid-phase extraction disks (Oasis silica disks), eluted with acetone. The final extract was then concentrated to 1 ml prior to analysis. Final quantification for all samples of atrazine was determined using a GCMS operating in ELI-Sim mode.

The particle-to-water partitioning coefficient is defined as the concentration of contaminant per gram of sediment to the concentration in 1 g of water. The empirical partitioning coefficient was derived from the in situ concentration of organic contaminants on water column particles divided by the aqueous concentrations. Previous research has also allowed for the optimization of both water column and soil extractions. Based on ¹³C-internal standards and spiked reference materials, recoveries were at 90–93 % with a detection limit of 1 ng/g.

A one-way ANOVA was employed to determine significant ($p < 0.05$) differences in water factors during flooded and nonflooded periods. When significant differences were detected, the ANOVA was followed by a Tukey's HSD post hoc test. Statistical analysis was performed using the SPSS for Windows version 16 Statistical Software (SPSS Inc., Chicago, IL).

3 Results

3.1 Water column concentrations and partitioning behavior

Monitoring of the Rio Grande began in the spring of 2010 in order to monitor the overall water quality of this region (dissolved oxygen (DO), nutrient levels, pH, flow, and total suspended matter (TSM)). These samples were then utilized for analysis of the contaminants of interest (triclosan, atrazine, ciprofloxacin). Assessment of pre- and post-flood concentrations within the river system was possible due to an ongoing monitoring program for the Rio Grande implemented by TAMU in the fall of 2009.

The floodwaters were significantly different than waters typically found in this region (Table 1). There was a significant decrease ($p < 0.01$) in the pH and DO ($p < 0.001$) during the flood. There was also a significant increase ($p < 0.05$) in both nutrients and TSM. Both nitrogen and phosphorous more than doubled and the TSM in the system was over five times as high compared to pre-flood conditions. Typical flow rates for the Rio Grande within the Laredo, TX, city limits range from 50 to 100 m³/s. The flow of the river during the flood exceeded 4000 m³/s with an average of almost 1300 m³/s for the month of July.

Table 1 Water properties of the Rio Grande

Sampling period	pH	DO (%)	Nitrogen (mg/l)	Phosphorous (mg/l)	Total suspended matter (mg/l)
Pre-flood May 2010–June 2010	8.1±0.2 a	89±4 a	2.03±0.12 b	0.13±0.06 b	148±34 b
Flooding July 2010	7.5±0.3 b	51±12 b	4.18±0.22 a	0.46±0.12 a	763±243 a
Post-flooding August 2010–December 2010	8.0±0.2 a	90±3 a	2.15±0.24 b	0.21±0.08 b	36±13 c

Differences in averages were determined using a one-way ANOVA; the letters indicated significant differences based on a post hoc Tukey’s LSD

The Rio Grande contained trace amounts of triclosan, atrazine, and ciprofloxacin during all flow conditions (Table 2). During the flooding of the Rio Grande, there was a significant increase ($p<0.01$) in the concentration of all three organic contaminants in both the water column and on suspended particulate matter in the system. In addition, we were able to determine that the partitioning coefficient significantly ($p<0.05$) increased for both triclosan and ciprofloxacin in floodwaters with a lower pH (Table 2). There was not a significant difference ($p>0.05$) in the partitioning of atrazine associated with changes in the water chemistry. Partitioning was determined as the concentration on 1 g of particulate to 1 g of water.

3.2 Contaminant distribution and subsequent behavior within the floodplain soils

In general, the highest concentrations of triclosan, atrazine, and ciprofloxacin were in the 0–2-cm surface depth of flooded quadrats (Figs. 2, 3, and 4). Of these flooded quadrats, those

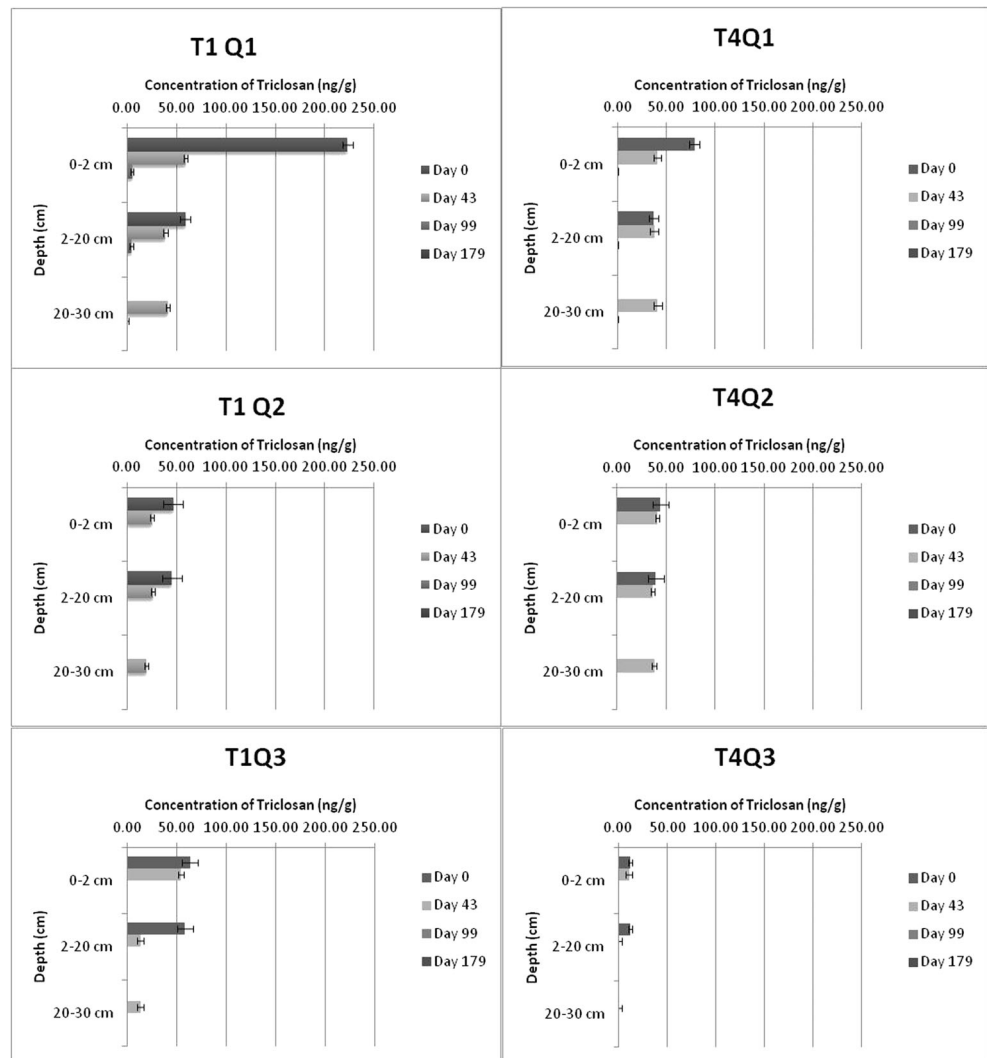
located nearest to the river contained the highest concentrations and the highest amount of particle deposition as indicated by visual inspection and particle size analysis. Contaminant concentrations decreased with depth. Concentrations of these compounds were generally higher at the LCC site, which is near an outfall for the sewage treatment plant in Nuevo Laredo, Mexico. The MR site received sediments from upstream of the city where agricultural lands using atrazine are commonly found. Therefore, the MR site was expected to contain higher concentrations of atrazine than the LCC site located nearer to the sewage outfall; this however was not what was observed. Low levels of particulate matter were found at the MR site, indicating a lower level of particle deposition and inundation overall. This also indicates that the overall particle loading may be the primary factor in determining contaminant concentrations during flood events, rather than proximity to contaminant sources. Organic contaminants were not detected in nonflooded soils. Therefore, the presence and behavior of these compounds are attributed to the flooding experienced in the affected quadrats.

Table 2 Average water column and sediment concentrations for all four sampling sites for the time periods before the flood, during the flood, and post-flood

Organic contaminant	Sampling period	Water column average (ng/l)	Suspended particulate average (ng/g)	Average partitioning coefficient (log k_d)
Triclosan	Pre-flood May 2010–Jun 2010	77±10	148±39	2
	Flooding July 9–July 23, 2010	112±52	763±102	4
	Post-flooding August 2010–December 2010	63±18	53±25	2
Atrazine	Pre-flood May 2010–June 2010	4±3	11±3	4
	Flooding July 9–July 23, 2010	17±5	32±20	4
	Post-flooding August 2010–December 2010	8±6	38±4	4
Ciprofloxacin	Pre-flood May 2010–June 2010	3±2	11±5	3
	Flooding July 9–July 23, 2010	32±15	112±44	4
	Post-flooding August 2010–December 2010	1±1	17±6	3

Partitioning coefficients were calculated (concentration on 1 g particle/concentration in 1 g water) in for individual samples then averaged here

Fig. 2 Concentrations of triclosan (ng/g) in the 50-m transects 1 (T1—LCC site) and 4 (T4—MR site) for the flooded quadrats Q1–Q3 showing concentrations at depth over time. Q1 was closest to the river and received the highest level of deposition during the flood



Over the subsequent 24 weeks, both triclosan and atrazine were significantly degraded (repeated measures ANOVA $p < 0.001$) and were not detected by week 24. The first quadrats at each site had the highest concentrations of triclosan and atrazine (Figs. 2 and 3); however, atrazine was only found in the first quadrat at the surface of the MR site. Triclosan at the surface layer of the LCC site was significantly higher than all other depths and time points ($p < 0.05$), while at the MR site, triclosan concentrations at both depths examined initially were similar. Atrazine concentrations were also similar at the surface layer and root zone immediately following the flood. The half-life for triclosan in this system was 23 ± 3 days, and for atrazine, it was 16 ± 1 days. Half-lives were calculated individually for all layers in which the compounds were present and then averaged. Triclosan did not decay between 0 and 6 weeks at the Mines Road site in all but one quadrat, then was not detected at 14 weeks; the half-life at this site was not calculable.

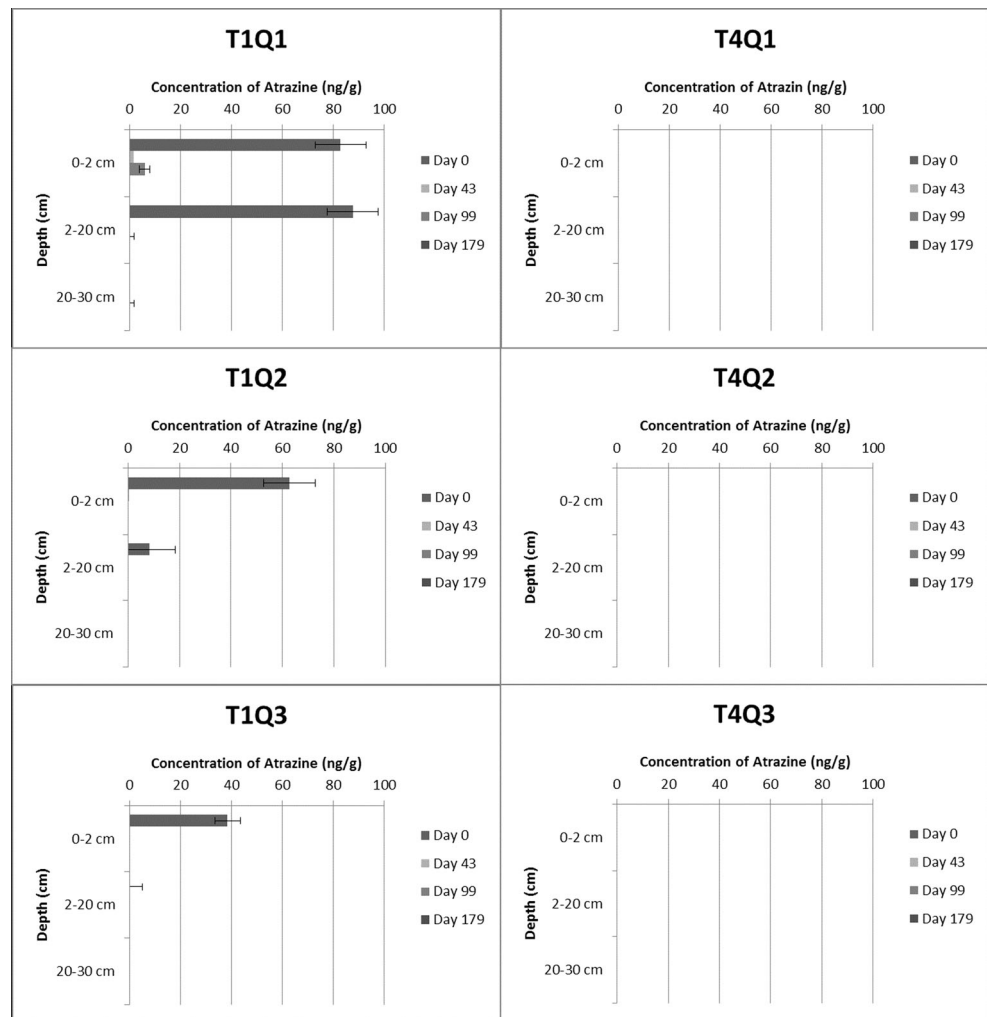
Overall, ciprofloxacin did not decay over the course of this study and remained present in these soils (Fig. 4) at

concentrations similar to those determined for the soils immediately following the flood (± 3 ng). Concentrations did not increase with depth following rain events occurring over the study period (Figs. 2, 3, and 4).

3.3 Physiochemical behavior over 6-month monitoring period post-flood

This study examined the in situ impacts of a flooding event on contaminant deposition and fate in a riparian ecosystem. Overall, soils at the LCC site showed a greater change in soil composition due to floodwaters when compared to the MR site. Riparian soils were chemically altered by the inundation of standing floodwaters with a significant decrease ($p = 0.0022$) in soil pH that was reduced to a mean of 7.8 in flooded soils immediately following the flood, as opposed to 8.2 in nonflooded soils. Soil pH at the MR site was not affected by flooding (see Tables 1Sa and 2Sa in the Electronic Supplementary Material). There was also a

Fig. 3 Concentrations of atrazine (ng/g) in the 50-m transects 1 (T1—LCC site) and 4 (T4—MR site) for the flooded quadrats Q1–Q3 showing concentrations at depth over time. Q1 was closest to the river and received the highest level of deposition during the flood

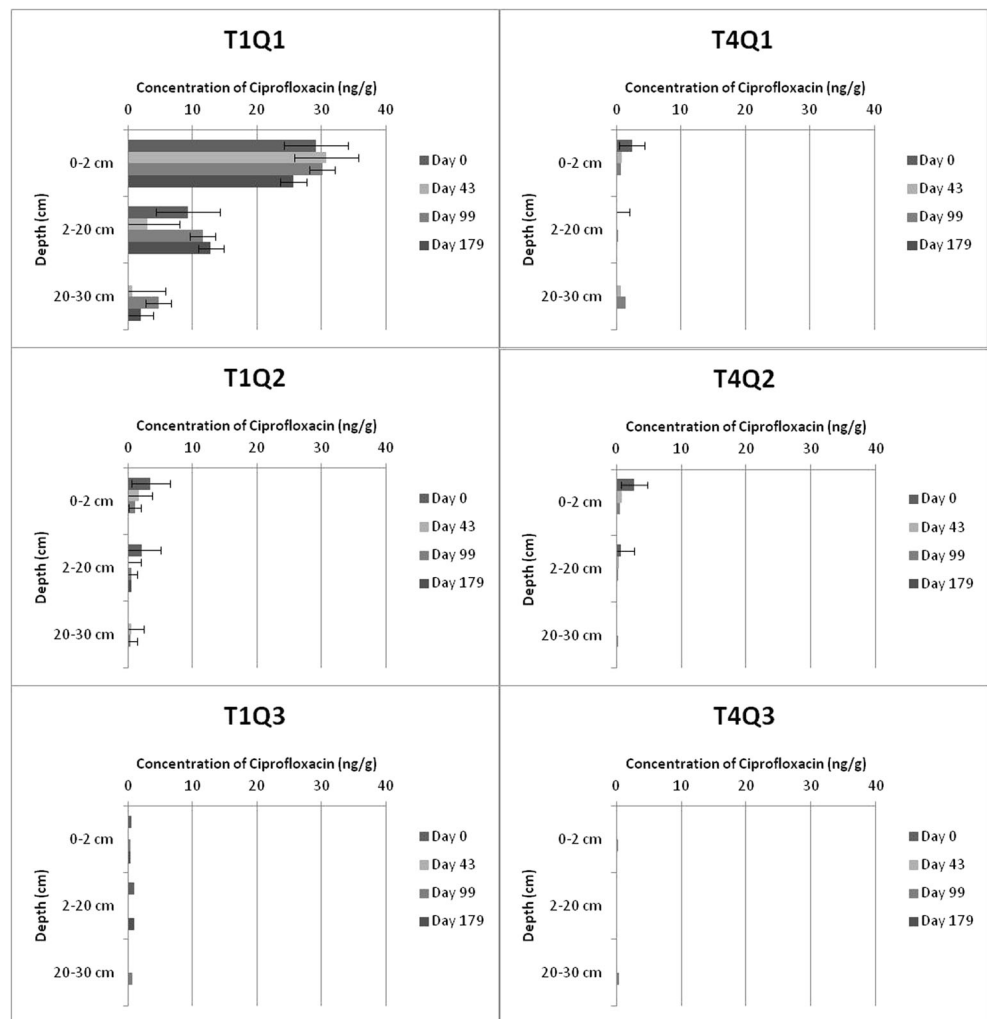


significant increase ($p < 0.0001$) in EC immediately following the flood at both sites (see Tables 1Sb and 2Sb in the Electronic Supplementary Material). However, flooding effects were more drastic at the LCC site with an EC mean of 0.98 dS/m in flooded soils and 0.23 dS/m in nonflooded soils; flooded soils were moderately saline and nonflooded soils were nonsaline as defined by Scianna et al. (2007). At the upper soil layers, mean soil EC at the LCC site decreased over time, while EC increased at the 20–30-cm deep soil layer, suggesting that salts eventually leached from the upper surface layers over the sampling period. The flooded surface layer became nonsaline by week 24. Salt deposition at the MR site was minimal as flooded soils were considered to be slightly saline (0.37 dS/m) and nonflooded soils were very slightly saline (0.28 dS/m). As observed at the LCC site, the mean soil EC in the quadrats closest to the river at the 0–2-cm surface layer were significantly higher in mean soil EC ($p < 0.01$) than all other quadrats immediately following flooding (week 0) and 6 weeks later. Soils of the first two quadrats nearest the Rio Grande at the LCC and MR

sites demonstrated a greater deposition of clay-sized ($< 2 \mu\text{m}$) particles at the surface layer (0–2 cm), while a higher proportion of clay-sized particles were found in the root zone (2–20 cm) of the LCC site compared to the MR site (Table 3). Based on the particle size analysis, all soils would be classified as silt except at the root zone of quadrat 6 (silt loam), and the surface layer of the first two quadrats at the MR site (silt loam). The CEC was highest at the surface of the first quadrat of the LCC site where higher concentrations of organics were also detected. Overall, there was not a significant change in mean CEC over time ($p < 0.05$) except in the first quadrats of each transect (data not shown).

All other soil parameters (organic carbon, nitrogen, phosphate, and soil moisture) did not differ significantly between flooded and nonflooded soils. At 14 weeks, differences between flooded and nonflooded soils were not significant for pH, EC, or CEC as observed initially. This demonstrated recovery of the system to baseline values, assumed to be equivalent to the nonflooded soils.

Fig. 4 Concentrations of ciprofloxacin (ng/g) in the 50-m transects 1 (T1—LCC site) and 4 (T4—MR site) for the flooded quadrats Q1–Q3 showing concentrations at depth over time. Q1 was closest to the river and received the highest level of deposition during the flood



4 Discussion

4.1 Sediment contamination and impacts on contaminant levels

Contaminants can be brought into floodwaters by various sources. In addition to floodwaters released from Amistad Reservoir, upstream point sources likely included runoff from industrial and agricultural lands adjacent to the Rio Grande that were impacted by the flood. Triclosan and ciprofloxacin are likely sourced from municipal and agricultural lands, while atrazine is most commonly found in agricultural farmlands. Sewage overflows occurred in both Laredo, TX, and Nuevo Laredo, Mexico, with more than 800,000 gals/day of raw sewage released from July 8 to 16, 2010 (LDH 2010). These municipal sources were likely the primary source of both triclosan and ciprofloxacin which resulted in higher concentrations in the water column found at sampling sites downstream of the lift stations. There are four primary fates for these contaminants within the flood waters: (1) they will remain aqueous within the water column; (2) they will be

adsorbed and deposited within the river sediments; (3) they will be adsorbed then deposited with sediments on floodplain soils; and/or (4) they will infiltrate floodplain soils with the flood waters, then remain in the soils, Fig. 5.

The partitioning coefficients (discussed above) show that the majority of the observed contaminants were adsorbed onto particles within the water column. Water column concentration increased as expected during the flood, with an increase in the partitioning coefficient of triclosan and ciprofloxacin. As pH increases these compounds will deprotonate, allowing them to associate with other cations within the water column and particle surfaces (Wilson et al. 2009). There was not an increase in the partitioning of atrazine. Partitioning of atrazine is more closely associated with the organic content of particles rather than the pH of the system (Basta et al. 1997); therefore, without a significant change in the organic content of particles in the Rio Grande floodwaters, partitioning did not increase.

Contaminated particles were then deposited onto the floodplain soils sampled in this project. Surface samples contained high levels of litter, usually indicative of soils with a high organic carbon content. A fine layer of newly deposited

Table 3 Particle size analysis and CEC by depth and quadrat along two 50-m transects (transect 1 at the LCC site and transect 4 at the MR site) immediately following the flooding of the Rio Grande in July 2010

Depth (cm) and quadrat ^a	LCC site (transect 1)				MR site (transect 4)			
	Particle size analysis			CEC cmol _c kg ⁻¹	Particle size analysis			CEC cmol _c kg ⁻¹
	>50 μm %	2–50 μm	<2 μm		>50 μm %	2–50 μm	<2 μm	
0–2 (surface layer)								
Q1	7	83	10	5.21	4	84	12	2.20
Q2	9	81	10	2.50	2	84	14	2.79
Q3	6	89	5	2.06	7	90	3	2.71
Q4	6	92	2	2.08	5	86	8	1.91
Q5	8	91	1	1.59	0	97	3	2.36
Q6	9	90	1	2.06	7	89	4	1.94
2–20 (root zone)								
Q1	9	82	9	2.21	5	91	4	2.11
Q2	5	91	4	2.30	9	86	5	2.71
Q3	10	87	3	1.91	9	89	2	2.50
Q4	11	85	4	1.75	7	88	5	2.80
Q5	10	88	2	1.66	2	95	3	1.65
Q6	21	78	1	1.71	9	88	3	2.11

Quadrats 1–3 were flooded, and quadrats 4–6 were not flooded

^aThe 20–30-cm depth was not sampled immediately following the flood

sediment covered both the topsoil and plants in the area. Within areas of dense plant cover, the sediment layer was up to 2 cm in depth in quadrats closest to the river, with scoured areas having as little as 1–2 mm of deposition. This increase in sediment was also apparent in the soil texture analysis, with an increase in clay-sized particles in flooded quadrats when compared to the nonflooded quadrats. Therefore, contaminant levels were highest at the surface (Figs. 2 and 3), yet the presence of contaminants throughout the soil profile indicates

that floodwaters inundated soil pore spaces followed by direct adsorption to soil particles at lower depths.

Overall, greater differences in organic contamination and impacted soil factors occurred in the first quadrat of each transect, which was closest to the river and under water for the longest period of time, increasing contaminant exposure. Further, these differences were more notable at the LCC site where contamination from sewage outfalls along with municipal runoff likely occurred. The LCC site is located at a bend in the Rio Grande which may have contributed to the additional flooding and particulate deposition at this site. Given that clay-sized particles appeared greater within the first two quadrats of both the LCC and MR site, these quadrats were likely those that had been flooded longer than the third quadrat examined at each transect. However, a higher infiltration of floodwaters occurred at the first quadrats of the LCC site when compared to the MR site, which coincides with contaminant levels.

4.2 Organic contaminant behavior within soils

Triclosan and atrazine were both found to degrade within the soils over a 6-month period with a half-life of 23±3 and 16±1, respectively. These results are similar to other studies indicating that the soil type and the method of contaminant deposition can affect the degradation rates for these compounds. In an agricultural field, the half-life of triclosan was 107 days

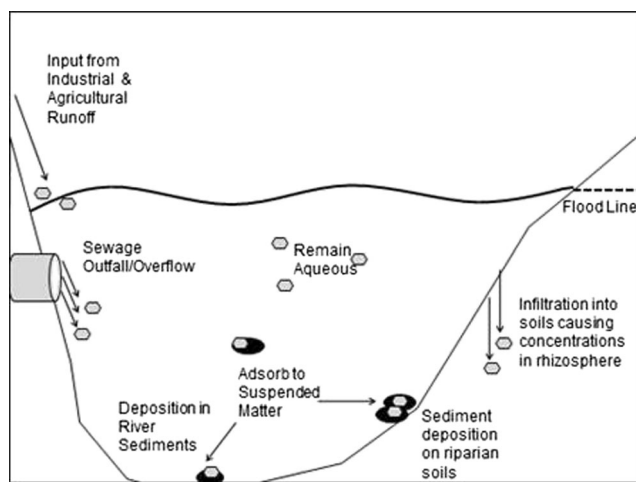


Fig. 5 System model for the fate of contaminants within the water column during a flood event

after a single biosolid application (Lozano et al. 2010), while the half-life of triclosan when applied as a solution was similar to that observed at the LCC site. Soils with a high pH (>7.4) have a short degradation half-life of 2 to 3 weeks due to the high bioavailability of triclosan and subsequent biodegradation in aerobic conditions (Ying et al. 2007; Xu et al. 2009; Carr et al. 2011). Ciprofloxacin likely sorbed to clay particles as observed with fluoroquinolones at moderately alkaline conditions during which ciprofloxacin becomes protonated (Nowara et al. 1997; Golet et al. 2003). Benchtop studies indicate that ciprofloxacin is generally persistent in sludge unless it is aerated or subjected to photolysis in aquatic systems (Burhenne et al. 1997; Halling-Sørensen et al. 2000, 2003; Pereira et al. 2007). Our data suggests that ciprofloxacin in soils after a flood will remain for at least 6 months. Long-term field experiments are needed to understand the persistence of ciprofloxacin and if disturbance of soils would affect its degradation. Further, the absence of changes in concentrations of all contaminants with depth over time, despite rain events, indicates that organic contaminants were not mobile in the system.

Previous studies have shown that the mobility of these compounds in soils is correlated to the combined effect of the CEC, EC, and pH of a system. In areas with a high pH and EC, triclosan has limited mobility in soils, as was shown in this study. Additionally, triclosan decayed within a month in this study as similarly found in other studies when triclosan-contaminated biosolids were applied when wet (Al-Rajab et al. 2009; Xu et al. 2009). Ciprofloxacin's behavior and bioavailability is also closely related to the CEC of a system as it is likely able to bind strongly to cations, thereby reducing the ability of a system to remove this contaminant (Golet et al. 2003).

5 Conclusions and managerial considerations

The completion of this project has provided a better understanding of the behavior of contaminants mobilized by flooding events and deposited onto soils. Our continued study of contaminant dynamics will greatly impact our understanding of agricultural lands as managed ecosystems. Here, we have shown that substantial quantities of organic contaminants, specifically herbicides from agricultural lands and antimicrobials from wastewater treatment plants/sewage lines, can be distributed to floodplains via particle adsorption and deposition. Additionally, this study of a natural flooding event has demonstrated that contaminants found at lower depths in floodplains are due to the initial infiltration of flood waters rather than leaching from post-flood particulate deposition. Our data indicates that triclosan and atrazine are undetectable between 6 and 14 weeks post-flood; however, ciprofloxacin remains in soils for at least 24 weeks with no vertical mobility.

Most agricultural lands are within the floodplain of major rivers in the USA (FEMA 2014). Periodic flooding may potentially allow for contaminants, such as those examined, to become available to commercial crops. In turn, this would constitute an indirect exposure to the people relying on these food sources. Further, the deposition of antimicrobials and persistence of these compounds may increase populations of antimicrobial resistant microbes. Floodwaters likely deposited microbes with some antimicrobial resistance, given that sources included sewage outfalls and wastewater effluent and may have influenced changes in the microbial community (not addressed here). We are now beginning to address behavior of organic contaminants and impact on microbial communities in agricultural soils due to the use of recycled water from municipal/industrial sources used for irrigation in nonfloodplain regions.

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