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Pharmaceutical and personal care products in tile drainage following land application of municipal biosolids

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ABSTRACT

Land application of municipal biosolids (sewage) is a common farming practice in many parts of the world. There is potential for transport of pharmaceuticals and personal care products (PPCPs) from agricultural fields to adjacent surface waters via tile drainage systems. In this study, liquid municipal biosolids (LMB) (total solids = 11,933 mg L^{-1}), supplemented with selected PPCPs and the fluorescent dye tracer rhodamine WT (RWT), were applied to tile drained fields using two land application approaches. Objectives included evaluating the relative benefits of land application practices with respect to reducing PPCP loadings to tile drains, evaluating PPCP persistence in tile water, and determining whether rhodamine WT can be used to estimate PPCP mass loads in tile. The PPCPs examined included an antibacterial agent used in personal care products (triclosan), a metabolite of nicotine (cotinine), and a variety of drugs including two sulfonamide antimicrobials (sulfapyridine, sulfamethoxazole), a β-blocker (atenolol), an anti-epileptic (carbamazepine), an antidepressant (fluoxetine), analgesic/anti-inflammatories (acetaminophen, naproxen, ibuprofen), and a lipid-regulator (gemfibrozil). Maximum observed PPCP concentrations in the spiked LMB were about 10^3 ng g^{-1} dry weight. PPCPs were shown to move rapidly via soil macropores to tile drains within minutes of the land application. Maximum observed PPCP concentrations in tile effluent associated with the LMB application-induced tile flow event were ~10^1 to 10^3 ng L^{-1}. PPCP mass loads, for the application-induced tile-hydrograph event, were significantly ($p<0.1$) higher for surface spreading over non-tilled soil (incorporation tillage occurring 20 h post-application), relative to aerating soil immediately prior to surface spreading using an AerWay® slurry deposition system. PPCP concentrations that were detected above the limit of quantitation (LOQ) in tile water during several precipitation-induced tile flow events that occurred post-application, included: triclosan (max. ~1.5×10^2 ng L^{-1}), carbamazepine (max. ~7×10^1 ng L^{-1}), atenolol (max ~4×10^1 ng L^{-1}), and cotinine (max ~2×10^1 ng L^{-1}). In spite of their presence in biosolids, the other PPCPs were not observed above LOQ concentrations during these events. PPCP concentrations were predicted from RWT concentrations over a 40 day study period. Tile

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Abbreviations: A, AerWay; CEC, cation exchange capacity; LMB, liquid municipal biosolids; LOD, limits of detection; LOQ, limits of quantitation; OC, organic carbon; PPCP, pharmaceutical and personal care products; RWT, rhodamine WT; SS, surface spread + incorporation; WWTP, waste water treatment plant.

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mass loads as a percent of PPCP mass applied to soil ranged from 4.2% ± SD of 9.2% to 7.1% ± 10.9% for the AerWay® system and surface spreading plus incorporation treatments, respectively.

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1. Introduction

Significant concentrations of human pharmaceuticals and personal care products (PPCPs) have been detected in municipal sewage, and some of these chemicals are resistant to removal during the sewage treatment process (Ternes, 1998; Miao et al., 2002; Khan and Ongerth 2002; Khan et al., 2004; Lindberg et al., 2005; Miao et al., 2005; Halden and Paull, 2005; Yang and Metcalfe, 2006; Joss et al., 2006). PPCPs can be discharged directly from municipal wastewater treatment plants (WWTPs) into the aquatic environment, or these compounds can be released indirectly following land application of sewage biosolids (Heberer, 2002; Nentwig et al., 2004; Sedlak et al., 2004, Glassmeyer et al., 2005; Heidler et al., 2006; Yang and Metcalfe, 2006; Kinney et al., 2006a). The widespread detection of various PPCPs in surface waters (Kolpin et al., 2002; Metcalfe et al., 2004; Brun et al., 2006) has fostered more focused scientific and regulatory attention on the sources, fate, and effects of PPCPs in the environment (Daughton, 2004).

Sewage biosolids are an inevitable by-product of the treatment of municipal wastewater. In the United States, it is estimated that the average waste water treatment plant (WWTP) produces 240 kg dry weight of biosolids per million litres of wastewater treated (Kinney et al., 2006a). The per capita production of treated biosolids in European Union (EU) countries is estimated to vary between 9 and 38 kg dry weight per annum (European Commission, 2001). The application of treated sewage biosolids onto agricultural land is a common farming practice (Joshua et al., 1998; Mantovi et al., 2005). The European Commission (2001) estimates that Ireland, Finland and United Kingdom, use the highest percentage of municipal biosolids for agriculture among the EU countries (i.e. >70%). The fraction of biosolids used as fertilizer in Denmark declined from 70% to 60% over 1995 to 2001 because of increasing regulations regarding product quality (Jensen and Jepsen, 2005). In the province of Ontario, Canada, about 120, 000 t (dry weight) of biosolids are applied annually to approximately 15, 000 ha of tiled and untiled agricultural land.

Tile drains are usually installed on agricultural land to promote drainage where natural field drainage can adversely affect crop production activities. Typically tile drains are located within 1 m of the soil surface, and are efficient at short-circuiting soil drainage waters to adjacent surface waters such as streams and rivers. In Ontario, approximately 1.3 million ha of land is tile drained, and this value is expected to increase at a rate of approximately 40,000 ha year^{-1} (Ball-Coelho and Brown, 2004). PPCPs have been detected in groundwater (Sacher et al., 2001; Heberer, 2002) and in fields that had been irrigated with treated wastewater (Pederson et al., 2005). Our previous studies showed that PPCPs can be transported in surface runoff from biosolid-amended fields (Topp et al., in press). To our knowledge, there have been no studies of the transport of PPCPs in tile drainage systems after application of biosolids onto agricultural fields. However, veterinary antibiotics, carried in animal wastes applied to fields in the United Kingdom, were reported to be preferentially transported through tile drains immediately following land application (Kay et al., 2004).

The risk of reduced water quality from the transport of microbial or chemical contaminants carried in the biosolids is managed through regulations that specify: suitable weather and soil conditions at the time of application, appropriate application methods and rates, and acceptable biosolid composition (Walker et al., 1994; Payne et al., 2001; National Research Council, 2002; Schut, 2007). Nevertheless, there is still a need to determine if currently mandated land application practices help protect surface and groundwater resources from biosolid-based contaminants, including PPCPs (Rogers, 1996; Akhand et al., 2006; Lapen et al., 2008).

The assessment and monitoring of PPCP fate in field settings is currently hampered by the expense and technical challenge of the analytical methods that are required to identify and quantify these compounds in environmental matrices (Sedlak et al., 2004; Miao et al., 2002). Tracers that mimic PPCP behavior but that are more easily and inexpensively detected could be useful as fate surrogates, as likened to the use of florescent tracers (e.g., rhodamine WT) to predict transport and fate of pesticides in aquatic systems (e.g., Sabatini and Austin, 1991; Fox et al., 1991, 2002).

In this study, LMB supplemented with selected PPCPs and the fluorescent dye tracer rhodamine WT, was applied to tile drained field plots using two distinctly different land application approaches (Lapen et al., 2008). Our study objectives were to: i) evaluate the relative benefits of two land application practices with respect to reducing PPCP loadings in tile drains; ii) evaluate the transport of different PPCPs from fields receiving biosolids via tile effluent, and iii) estimate in an empirical manner, PPCP tile mass loads over the study period using continuously monitored rhodamine WT tracer as a PPCP surrogate.

2. Materials and methods

2.1. *Study site and LMB land application methods*

The study was conducted in Winchester, Ontario, Canada (latitude 45°03′ N, longitude 75°21′ W) in fall 2005 (October to December 2005) on a silt-clay loam soil (Table 1). Eight plots (six treatment plots and two control plots); each 100 m length (length of tile drain contributing area) centered over tile lines (100 mm diam. plastic tiles for treatment plots and 100 mm diam. clay tiles for control plots) were utilized in this study (Lapen et al., 2008). The control plots were located on an adjacent field that was hydrologically isolated from the treatment plots. Tiles were approximately 0.8 m below the surface at their deepest point along the plots. Tile discharge was monitored at plot outflow locales, and piezometer nests were placed in each plot representing intake depths of 0.6, 1.2, and 2 m below surface. A meteorological station at the site

Table 1 – Selected North Gower clay loam soil properties

Property	0–0.15 m	0.30–0.50 m
Clay (%)	38	42
Silt (%)	41	48
Sand (%)	21	10
OC (%)	2.1	0.5
pH (H_20)	6.6	6.8
CEC (me 100 g^{-1})	20	26

provided data on rainfall depth among other meteorological parameters.

Calibrated tipping bucket systems were used to measure tile discharge, and calibrated ISCO 6712 (ISCO Inc., Lincoln, NE) automatic water samplers fitted with Teflon intake line were used to collect tile water effluent. The 1 L ISCO sample bottles were lined with Teflon bags. The bags and bottles were cleaned after each collection event. ISCO liquid level actuators (Model 1640) were used to trigger the ISCO 6712 sampling programs on a rain event basis since tiles were running continuously over the study period. The actuators were set in small rainfall collectors to actuate once rainfall reached 5-mm depth. For the control plots, tile discharge and tile effluent sampling systems were set up according to methods described in Akhand et al. (2006). The ISCO water sampling programs were set to collect water when triggering occurred, every 15 min for 45 min post trigger, then every 30 min for 120 min, then every hour for 5 h, and the remaining samples were collected at 2-h intervals. However, at LMB application time, samples were collected manually every 15 min starting 30 min before application to 2 h post-application. Water samples collected for PPCP analysis during specific tile flow events, were those that appeared visually to be most turbid. Additional monitoring details are given in Lapen et al. (2008).

For this study, a common rate of LMB application (93,500 L ha^{-1}) using two distinctly different land application methods was employed. There were three plot replications for each of the two application treatments, with one control (no LMB applied) plot per treatment. The application approaches consisted of: i) AerWay SSD (Subsurface Deposition slurry applicator) (Holland Equipment Limited, Norwich, Ontario, Canada) system, which was designated as treatment A, and ii) LMB spreading on the soil surface (designated as treatment SS) followed by incorporation of the LMB within 24 h post-application using a Kongskilde vibro-shank cultivator, (Kongskilde, Exeter, Ontario, Canada). The AerWay SSD system surface-applies slurry close to the ground immediately following the pass of rolling tines that affect aerator-type tillage of the soil (Bittman et al., 2004). The AerWay SSD unit used in this study was mounted on the back of a slurry tanker that was pulled by a tractor. The nominal tillage

Table 2 – PPCPs and RWT uses and concentrations in LMB and tile water (ng L^{-1}) pre-application

Classes of PPCPs and RWT	Application	Pre-spike PPCPs in LMB (ng g^{-1} dw)	Post-spike PPCPs in LMB (ng g^{-1} dw)	Pre-spike PPCPs in LMB (ng L^{-1})	Post-spike PPCPs and RWT in LMB (ng L^{-1})	Pre-Application Tile Conc. (ng L^{-1})	PPCPs LOD, LOQ (ng L^{-1})
Acidic drugs							
Acetaminophen[a] (D3)	Analgesic/antipyretic	NA	1164[b]	NA	4475[b]	Below LOD	11, 35
Naproxen[a] ($^{13}C_1$,D3)	Analgesic/NSAID	NA	477[b]	NA	1835[b]	Below LOD	4, 14
Ibuprofen (^{13}C3)	Analgesic/NSAID	NA	1524[b]	NA	5863[b]	Below LOD	6, 21
Gemfibrozil[a] (D6)	Lipid regulator	NA	461[b]	NA	1772[b]	Below LOD	5, 16
Neutral/base drugs							
Carbamazepine (D10)	Anticonvulsant	673 ± 76	697 ± 24	2592 ± 294	2682 ± 92	Below LOD	2, 5
Cotinine (D3)	Metab. of nicotine	90 ± 16	111 ± 9	347 ± 62	427 ± 36	Below LOQ	1, 3
Fluoxetine(D5)	Antidepressant	83 ± 18	59 ± 3	318 ± 70	228 ± 10	Below LOD	3, 11
Beta-blocker							
Atenolol[a] (D7)	Beta-blocker drug	9 ± 0.6	43 ± 6	35 ± 2	166 ± 22	Below LOQ	2, 8
Anti-microbials							
Sulfamethoxazole[a] (^{13}C6)	Antimicrobial	4 ± 0.5	22 ± 1	15 ± 2	84 ± 4	Below LOD	4, 14
Sulfapyridine (^{13}C6)	Antimicrobial	ND	25[b]	ND	97[b]	Below LOD	7, 22
Antibacterial							
Triclosan (^{13}C12)	Antibacterial personal care product	NA	1007 ± 54	NA	3872 ± 206	Below LOQ	6, 19
Water tracer							
Rhodamine WT	Tracer	NA	NA	NA	500,000 to 14,000,000[c]	900 to 1500	500

a = PPCP spiked in LMB, b = estimated from tile effluent using mixing equations, c = range observed post-spike, LOD = limits of detection, LOQ = limits of quantitation, NA = Not analyzed, ND = Not detected.
The analytical limits of detection (LODs) and limits of quantitation (LOQs) are also provided for PPCPs and RWT (ng L^{-1}) in tile water. Standard errors are given as ± and, denoted in parentheses for each compound, are the stable isotope surrogate standards that were spiked into the sample as an internal standard for quantitation of the native analyte.

Table 3 – Breakthrough of LMB to tile and times of LMB application for each treatment plot

Treatment	Breakthrough (minutes after application)	Time of first LMB application pass (Julian day)
T1(A)	11	294.588
T2(SS)	3	294.569
T3(A)	9	294.657
T4(SS)	39	294.547
T5(A)	10	294.631
T6(SS)	16	294.520

depth for the AerWay SSD was 0.13 m (determinations of need for ballast were made immediately before application (Mclaughlin et al., 2006)), and the tines were set to a 10° angle to augment tillage action and soil pocket formation (Turpin et al., 2007). The surface spreading treatment was conducted using the AerWay SSD by depositing the LMB within 0.5 m above the surface, but with the tines lifted above the ground to avoid tillage action. Subsequent tillage of the LMB over the SS area was conducted around 20 h after application at an approximate incorporation depth of 0.1 m. The anaerobically digested LMB, which was obtained from a municipal WWTP that handles the waste from about 20,000 people, was trucked to the field site in nurse tankers fitted with ports and pumps to mix tanker slurry. Sampling of raw LMB from the LMB nurse tanker was conducted after prolonged tanker mixing had occurred and when the tanker was full, two thirds full, and one third full. All samples were collected in Teflon bottles.

2.2. *Chemicals*

Naproxen, ibuprofen, gemfibrozil, acetaminophen, cotinine, carbamazepine, sulfamethoxazole and atenolol were purchased from Sigma-Aldrich (Oakville, ON, Canada), and triclosan was obtained from Wellington Laboratories (Guelph, ON). Acetaminophen-d3, gemfibrozil-d6, cotinine-d3 and atenolol-d7 were purchased from C/D/N Isotopes Inc. (Pointe-Claire, QC, Canada). Carbamazepine-d10, naproxen-13C1, cotinine-d3, ibuprofen-13C3, sulfamethoxazole-13C6 and triclosan-13C12 were purchased from Cambridge Isotope Laboratories (Andover, MD, USA). The purity of all chemicals was >98% according to the

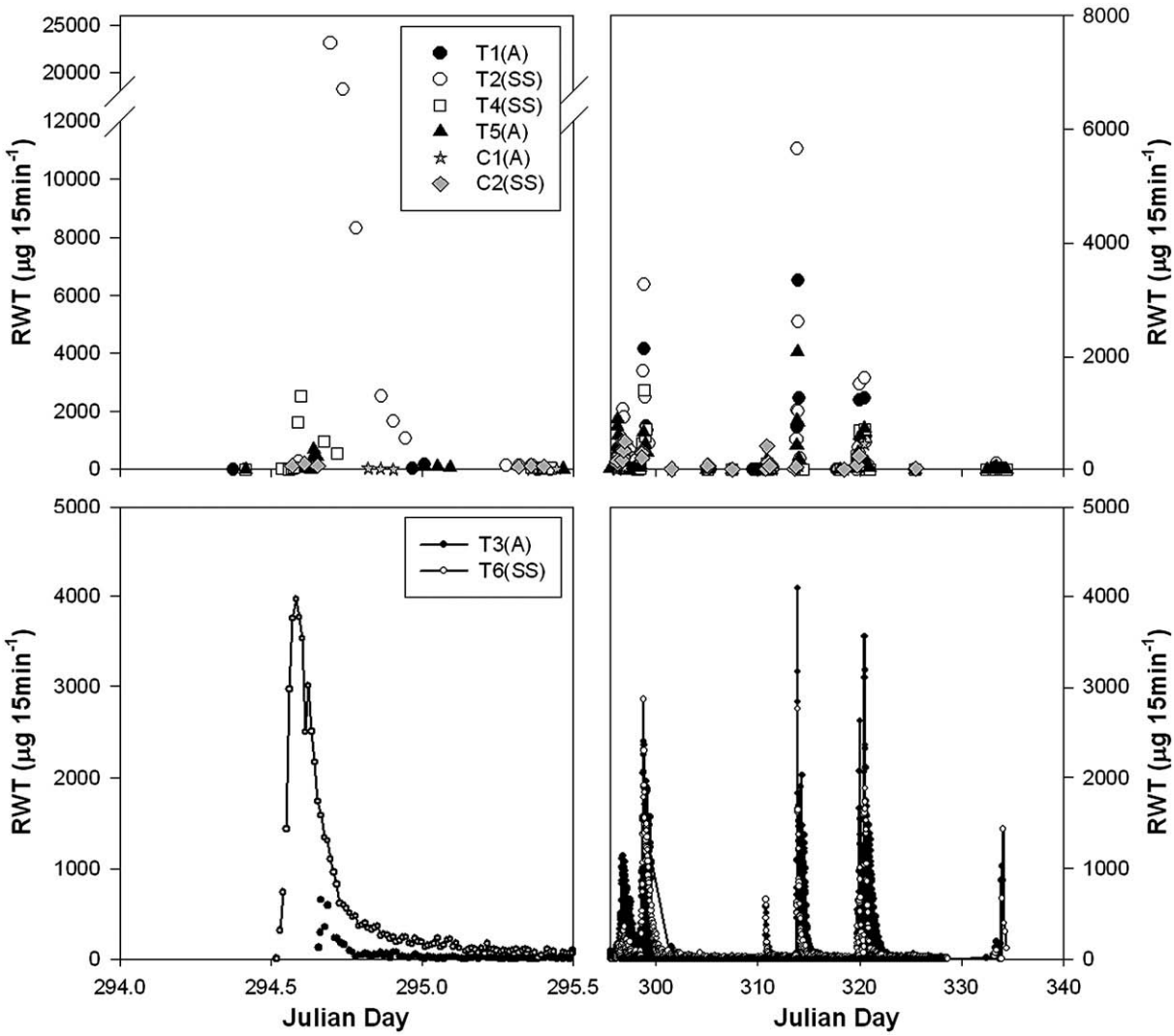


Fig. 1 – Rhodamine WT mass loads for LMB-induced tile hydrograph event, and remainder of study period.

suppliers. Rhodamine WT was obtained as a 20% solution from Keyacid Rhodamine WT liquid (Keystone Aniline Co., Chicago, IL, Product # 703-010-27).

2.3. PPCPs

Model chemicals from five classes of PPCPs were analyzed in LMB and in tile water, including 4 acidic drugs, 3 neutral/base drugs (includes a metabolite of nicotine), 2 sulfonamide antimicrobials, a β-blocker drug, and an antibacterial, triclosan (Table 2). All PPCPs examined were expected to be found in the applied LMB, given their occurrence in treated effluents from other WWTPs in Canada (Metcalfe et al., 2004). However, for detection/tracking purposes, some target compounds were supplemented (spiked) to nurse tanker LMB. Circulation pumps fitted to the nurse tanker, were used for mixing the LMB prior to land application. Chemicals spiked into the LMB were dissolved or suspended in 3 L of methanol, and this was dispensed into the nurse tanker at the field site. The targeted LMB spike concentrations for atenolol, naproxen, gemfibrozil, and sulfamethoxazole were 8800 ng L^{-1}, and that for acetaminophen was 87,000 ng L^{-1}.

All tile water samples and LMB (2 L for each sample) were processed immediately after collection. The methods used to prepare tile water samples for PPCP analysis have been described previously (Topp et al., in press), except that particulate materials were not removed from the samples prior to solid phase extraction. Each aqueous sample was divided into five aliquots of 250 mL, with each aliquot corresponding to one of the classes of PPCPs to be analyzed (Table 2). After adjustment of the pH according to the class of compound to be extracted, stable-isotope labelled surrogates (Table 2) were spiked into the samples at nominal concentrations of 100 ng L^{-1}. The five analyte classes were extracted by solid-phase extraction (SPE) with either HLB (Waters, Mississauga, ON, Canada) Oasis or MCX cartridges, as described in Topp et al. (in press). Extraction efficiencies for all analytes from water are >75%.

Spiked LMB was centrifuged with a desk-top centrifuge, about 5 g (wet weight) of the solids material was removed from the centrifuge tube, and freeze-dried. A subsample of approximately 1 g (dry weight) of freeze-dried material was necessary for extraction of all analyte classes, except for triclosan, which required only approximately 0.1 g of material. Extraction of the freeze-dried material was conducted by Pressurized Liquid Extraction (PLE) using an ASE 300 accelerated solvent extractor (Dionex, Oakville, ON). The stable isotope surrogates were added to the material in the stainless steel extraction thimbles prior to PLE. The extracts were enriched for the target analytes by passing the analytes through SPE cartridges. The conditions for PLE and the SPE enrichment method for neutral drugs were previously described by Miao et al. (2005). The methods for the preparation of LMB samples for analysis of triclosan were previously described by Chu and Metcalfe (2007). The extraction efficiency for triclosan from LMB is >95% (Chu and Metcalfe, 2007), and for the neutral analytes, extraction efficiencies from LMB are >80% (Miao et al., 2005).

The methods used for the extraction and enrichment of the sulfonamide antibiotics (i.e. sulfamethoxazole, sulfapyridine) have not been described previously. The PLE extraction conditions were: prefill method; solvents, 0.05 M phosphoric acid (pH 2.0) and methanol (50:50, v v^{-1}); equilibration, 5 min; static time, 5 min; flush volume, 100%; purge time, 120 s; static cycles, 2; temperature, 25 °C. The extract was poured into a 250 mL glass beaker and the methanol was allowed to evaporate by placing it overnight under a fume hood. After evaporation, the remaining aqueous matrix was diluted with 250 mL Milli-Q water, and this was enriched by SPE using an HLB* Oasis extraction cartridges. The SPE cartridge was pre-conditioned with 6 mL methanol and 10 mL milli-Q water (pH 3.0). The pH of the aqueous extract was adjusted to pH 4.0 with 3.5 M H_2SO_4, The extracts were passed through the SPE cartridges at a rate of approximately 10 mL min^{-1}. Once the sample had passed through the cartridge, the sample container was rinsed with approximately 10 mL of Milli-Q water (pH=4.0) and the rinsings were passed through the cartridge. The cartridge was then aspirated for one minute to remove residual water, and then the cartridge was charged with 3 mL of methanol, which was allowed to stand in the cartridge for 10 min before elution. The cartridge was eluted with another 3 mL of methanol, and then the cartridge was eluted with 3 mL of 2% NH_4OH in methanol. The extract was evaporated using a vacuum centrifuge to 0.1 mL and reconstituted in 50:50 methanol/water to a volume of 0.5 mL. To determine extraction efficiencies, freeze-dried LMB

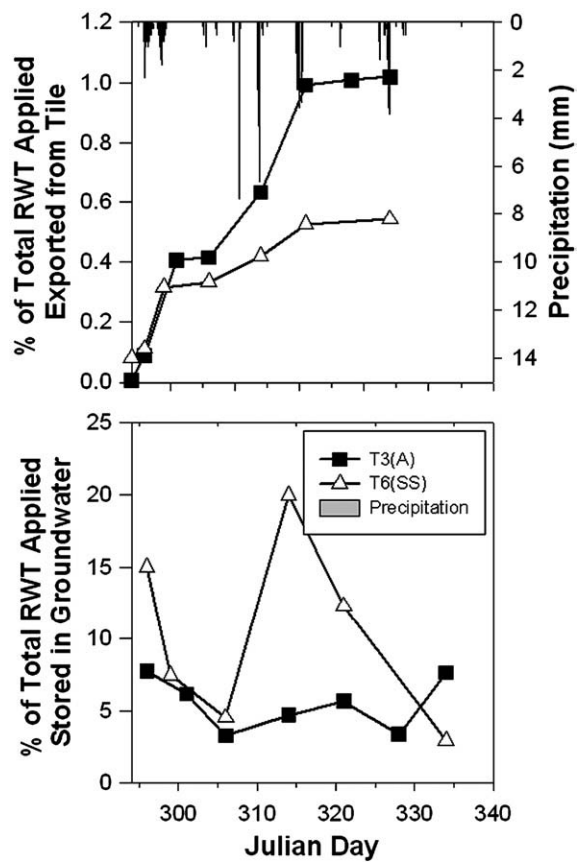


Fig. 2 – Estimate of rhodamine WT mass balance components over the study period, based on RWT measured in tilewater and groundwater. Groundwater storage was determined at each groundwater sampling time, and RWT tile export was determined at each of these sampling times as a cumulative percentage of total RWT applied to the tile, from application.

from a municipal WWTP located in Peterborough, Ontario, Canada, was spiked with the two sulphonamide antibiotics. The mean efficiencies of extraction ($n=3$) were 67% for sulfamethoxazole and 62% for sylfapyridine.

The target compounds (Table 2) present in extracts from tile water and spiked LMB were analyzed by liquid chromatography with electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS) as detailed in Topp et al. (in press). Briefly, the analytes were detected by monitoring in either negative or positive ion mode with multiple reaction monitoring (MRM). The acidic pharmaceuticals, atenolol, and triclosan were analyzed with a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, U.K.) fitted with an electrospray interface (ESI). The neutral pharmaceuticals and sulfonamide antimicrobials were analyzed with a QTrap mass spectrometer (MDS Sciex, Toronto, ON) equipped with an atmospheric pressure chemical ionization (APCI) ion source.

A series of external standards were prepared with different concentrations of the target analytes and fixed concentrations (50 ng mL^{-1}) of the analyte surrogates. The concentrations of the analytes were determined by comparing the response to each analyte in the samples to the responses to each analyte in the external standards over the range of a calibration curve. Note that this approach adjusts the quantitative data to compensate for efficiencies of extraction <100% and enhancement or inhibition of the signal due to the effects of the sample matrix. These response data were adjusted according to the relative ratios of the responses to the stable isotope surrogates in the sample and external standard. Blanks were prepared by spiking Milli-Q water with labelled surrogates, and extracting and analyzing them as described previously. In the sample blanks, all analytes were below detection limits.

The Limits of Detection (LODs) and Limits of Quantitation (LOQs) were determined for each analyte in an aqueous matrix using methods detailed in Topp et al. (in press). Briefly, these parameters were estimated by preparing simulated tile water samples in the laboratory in triplicate experiments. The extracts were prepared and analyzed as described above, and the LODs and LOQs were calculated as, respectively, 3× and 10× the standard deviation ($n=3$) of the baseline LC-MS/MS response monitored at the retention time for each analyte. The LOD and LOQ concentrations are listed in Table 2. The methods for the analysis of selected analytes in water were validated through inter-laboratory comparisons conducted with two other laboratories in Europe. Analysis of surface water collected from the Rhine River in Germany and extracted within 96 h of collection gave results for carbamazepine and atenolol which were within ±5% of the concentrations reported by the two other laboratories.

2.4. *Rhodamine WT*

Rhodamine WT (RWT), an adsorptive fluorescent xanthene dye, is often used as a tracer to characterize groundwater flow behavior, as well as a surrogate for waterborne organic pollutants in fate and transport studies (Vasudevan et al., 2001). RWT adsorption characteristics will vary according to a variety of site-specific soil chemical/physical properties (Smart and Laidlaw, 1977; Everts and Kanwar, 1994; Allaire-Leung et al., 1999). Thus, we attempted to evaluate if there were field-based relationships between RWT and PPCP concentrations in tile effluent, following LMB application, for the purpose of using continuously monitored RWT to help estimate study period tile mass loads of PPCPs.

Immediately prior to field application of biosolids, RWT was added to the LMB nurse tanker and subsequently mixed as described for spiked PPCPs. The target concentration was 8.5 mg L^{-1}; a value selected to ensure RWT was detectable in diluted phase in tile drainage and groundwater. YSI 6600 sondes (YSI Inc., Yellow Springs, Ohio, USA) were installed at tile effluent monitoring sites according to Lapen et al. (2008). Two of these sondes were fitted with YSI 6130 optical RWT sensors (i.e., T3 (A) and T6 (SS)). Data were recorded every 15 min. Control plots did not have sonde monitoring. RWT concentrations of diluted LMB (pre- and post-spike), tile water samples, and ground water samples (RWT concentrations derived from water collected from the piezometers) were measured using a hand-held YSI 600 OMS (optical monitoring system) with a YSI 6130 optical RWT sensor. In addition, a hand-held WQ770 Global water turbidimeter (Global Water Instrument Inc, Geneq, Inc., Montréal, QC, Canada) was used to measure turbidity for each discrete LMB, tile, and groundwater sample. The RWT sensors were calibrated using a 3-point calibration procedure, and all readings were automatically temperature compensated. The mass of RWT applied to each field plot (area = 1500 m^2) was determined from measurements of total LMB volume applied to the field plot (Lapen et al., 2008), and the RWT concentration of the LMB. RWT mass loads from T3(A) and T6(SS) was estimated using YSI 6600 sonde tile RWT concentration data and tile discharge measurements made every 15 min. For determination of RWT mass groundwater storage, it was first assumed that RWT did not infiltrate below 1.7 m depth from surface (assumed to be semi-impermeable (Lapen et al., 2008)), and that the porosity of the soil above 1.7 m was 0.44 m^3 m^{-3} (Lapen et al., 2004). Changes in the water table depth (used to determine the volume of groundwater) were determined using coupled evaluations of measured piezometric head, hourly well-logging on site using a Global Water Model- WL15X-015 (Global Water Instrument Inc., Gold River, CA) water level recorder, time domain reflectometry (TDR) measures of soil water content, and tensiometry (Lapen et al., 2008). Thus, the mass of RWT in groundwater was estimated by multiplying the volume of groundwater above 1.7 m by RWT concentrations of groundwater collected from the 1.2 m piezometer and, if applicable, the 0.6 m piezometer.

2.5. *PPCP mass load estimates*

For post-application PPCP tile mass load calculations, only PPCPs above LOQ concentrations were considered. For these samples, pre-application background PPCP concentrations were subtracted prior to mass load calculations. In order to provide semi-quantitative approximations of PPCP tile mass loads for the study period, the continuous measurements of RWT concentrations derived from the YSI 6600 optical sensors on tile treatment plots T3(A) and T6(SS) were used to predict PPCP concentrations. Linear regressions were separately used to predict PPCPs from RWT (15 min interval) for: i) data collected the day of land application (i.e., LMB-induced tile hydrograph

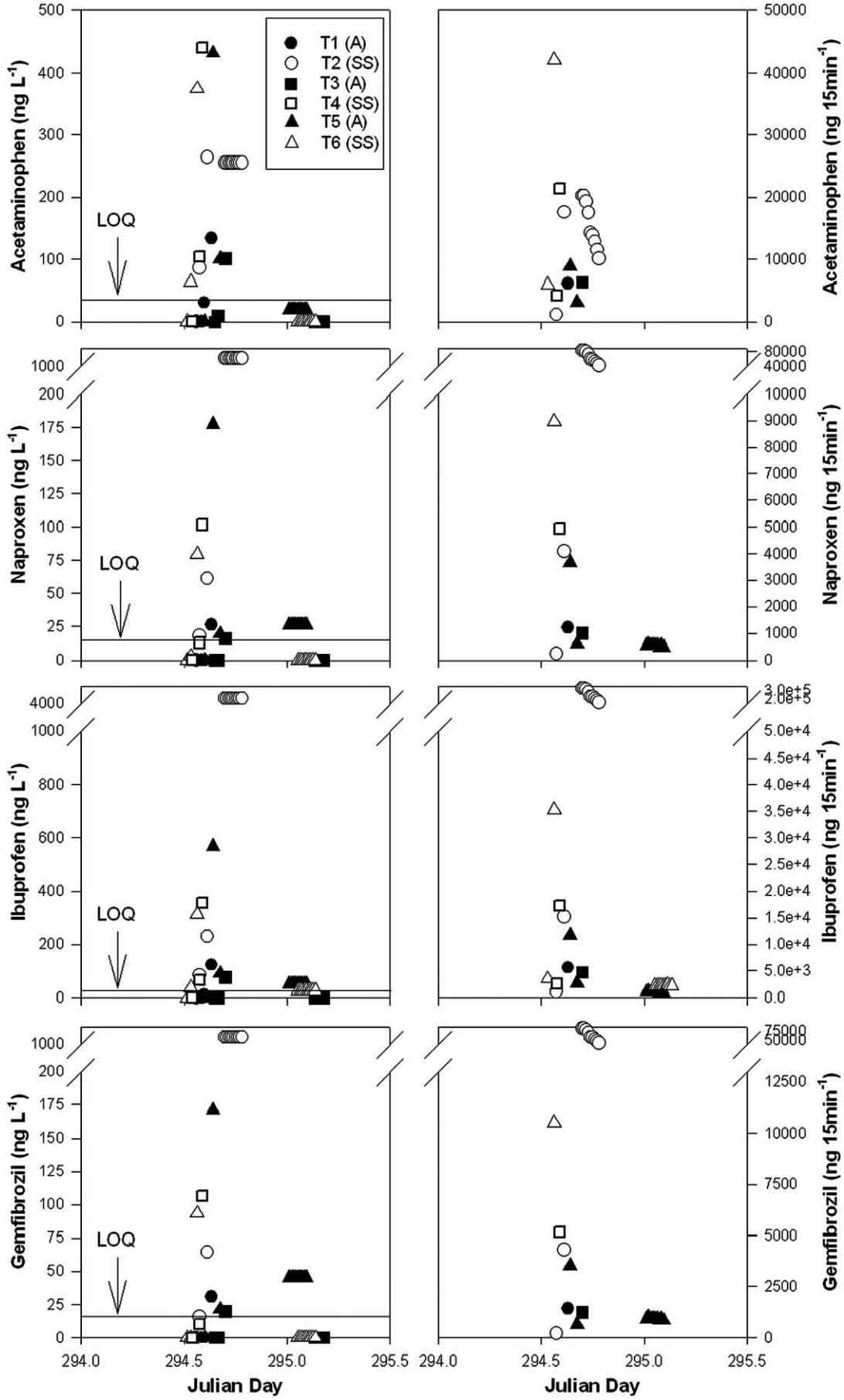


Fig. 3 – Acidic drug concentrations and mass loads in tile water for LMB application-induced tile discharge event.

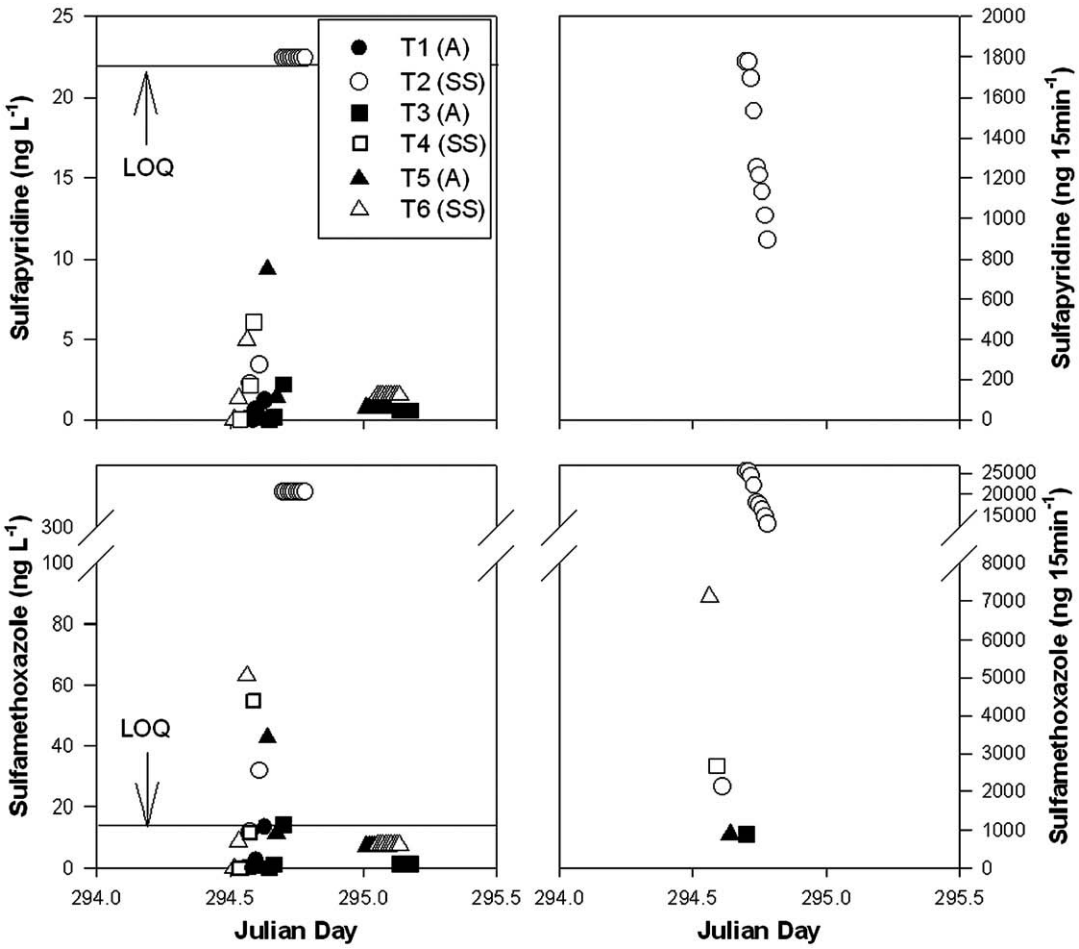


Fig. 4 – Sulfonamide concentrations and mass loads in tile water for LMB application-induced tile discharge event.

event), and; ii) tile water data collected over the remainder of the study period. This regression partitioning was conducted to account explicitly for differences in tile flow producing processes as related to application-induced tile flow and precipitation-induced tile flow (Akhand et al., 2006; Lapen et al., 2008).

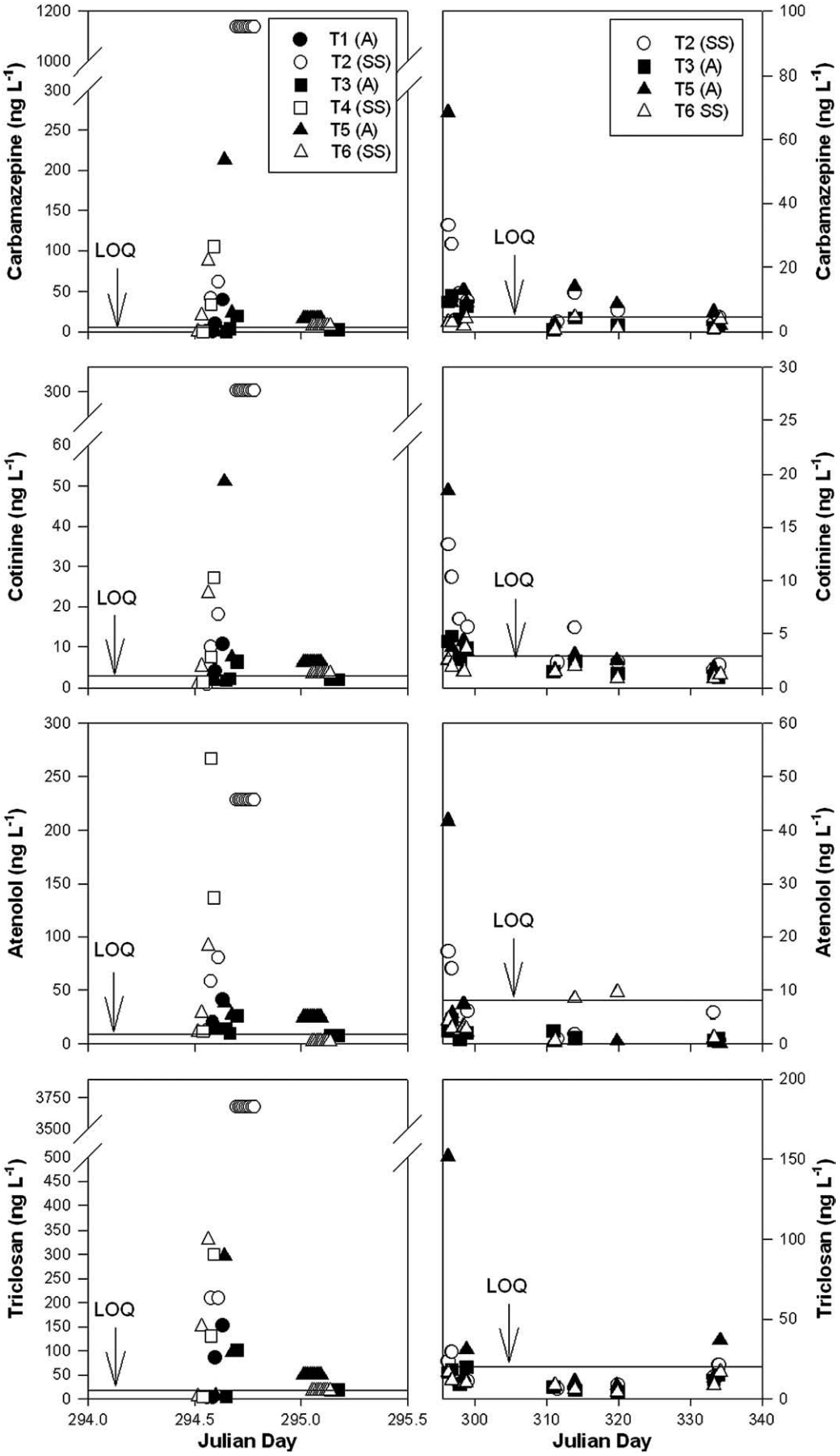
3. Results

3.1. *General*

The LMB ($N=3$ replicates) had the following key properties: Specific conductivity, 5450 μs cm^{-1}; pH, 7.6; alkalinity, 2780 mg L^{-1} (as $CaCO_3$); total solids, 11,933 mg L^{-1}; total solids (ash), 4880 mg L^{-1} total volatile solids 5710 mg L^{-1}. The material had a high fluidity, based on the relatively low total solids content (Malgeryd and Wetterberg, 1996), and is representative of other LMB used in Ontario (Schut, 2005). Total precipitation for the study period was 124 mm, with a maximum rainfall rate of 7.4 mm h^{-1} observed on Julian Day (JD) 310. Soil temperature for the study period averaged 8 °C (ranging from 5 to 12 °C) at 60 cm depth and 5 °C (ranging from −1 to 10 °C) at 10 cm depth. The application took place on JD 294 and the first post-application rainfall that stimulated tile flow began at JD 295.98. The time it took for the LMB to reach the tiles ranged between 3 and 39 min (Table 3). The transient soil physical conditions at the time of application are described in detail in Lapen et al. (2008), but generally the soil water content for the 0.6 to 0.9 m depth increment was near saturation and all tiles were flowing. The soil above 0.6 m depth was unsaturated at the time of application.

3.2. *Rhodamine WT*

Concentrations of RWT in the raw LMB ($N=3$ replicates) ranged between 0.5 to 14 mg L^{-1}, as determined via diluting the samples to ranges where sensing readings were considered accurate (Smart and Laidlaw, 1977; Edwards et al., submitted for publication). Since these sample concentrations bracketed the value strived for during the RWT spiking operation (8.5 mg L^{-1}) we assumed that the LMB RWT concentration was 8.5 mg L^{-1}. In preliminary experiments Edwards, et al. (submitted for publication), found that underestimations of RWT increased with an increase in LMB total solid concentrations in LMB/water mixes. However, for this study, continuous optical sensing of RWT in T3 (A) and T6(SS) was not hampered unacceptably by these limitations for the ranges of RWT concentrations observed (<30 μg L^{-1}) (periodic lab checks of diluted samples during peak


T1 (A)
T2 (SS)
T3 (A)
T4 (SS)
T5 (A)
T6 (SS)
T2 (SS)
T3 (A)
T5 (A)
T6 SS)
LOQ
Carbamazepine (ng L-1)
Cotinine (ng L-1)
Atenolol (ng L-1)
Triclosan (ng L-1)
Julian Day
Julian Day

biosolid-based discharge) (Smart and Laidlaw, 1977)) and maximum observed LMB-based total solid concentrations in tile effluent (<270 mg total solids L^{-1}).

For the control plots, RWT sensing indicated RWT mass loads averaged 100.3 (standard error = 17.45) μg 15 min^{-1} over the entire monitoring period (Fig. 1). This was a result of nominal background florescence since no RWT was applied to control plots. The SS treatment RWT tile mass loads for JD 294–295 were significantly ($p<0.1$) higher than those for the A and control treatments as determined via *t*-tests (SYSTAT v. 10, SPSS Inc., Chicago, IL); T2(SS) having relatively higher RWT mass loads. However for data collected for days ≥ JD 296, there was generally more parity between treatments with respect to rain induced tile RWT mass loads, and except for T2(SS), peak observed RWT mass loads were generally higher than those associated with the LMB-induced tile hydrograph event. For the remainder of the study period (JD ≥ 296), T3(A) RWT mass loads were significantly ($p<0.1$) higher than those for T6(SS). However, there were no significant ($p>0.1$) differences between A and SS RWT mass loads for the other treatment tiles. The mass load of RWT as a percentage of the amount applied to the plot (Fig. 2), was slightly greater for T6(SS) than T3(A) for the first few days following application. The greatest increases in RWT as percent of mass applied to T6(SS), occurred between application and approximately JD 300, after which, percentage increases over time were relatively smaller. This was not the case for T3(A) which showed fairly consistent percentage increases between application and JD 322, after which, trends stabilized. Fig. 2 suggests overall that a majority of the RWT applied to the plots (generally over 80%) was either sequestered or degraded in the soil, since the mass of RWT detected in groundwater ranged from 20% to less than 5% of the applied RWT, depending on water table depth below surface.

3.3. PPCPs

The concentrations of PPCPs in LMB before and after spiking are summarized in Table 2. The concentrations of acidic drugs in the LMB could not be determined due to low recoveries of this class of compound from the biosolids. The PPCPs that were spiked into LMB included acetaminophen, atenolol, naproxen, gemfibrozil, and sulfamethoxazole. It is unclear why the nominal concentrations of target compounds spiked into the LMB were not achieved in the measured concentrations, but causes could include poor mixing in the tank (despite nurse tank mixing prior to land application), chemical precipitation, or problems with obtaining representative samples of LMB. PPCP concentrations in tile water prior to LMB application (and in control plots) are given in Table 2 and indicate that all concentrations were below the LOQ. For all post-application observations, all control plot PPCPs concentrations were below the LOQ.

Fig. 3 indicates that the greatest concentrations and mass loads for the acidic drugs naproxen, ibuprofen, and gemfibrozil were exclusively associated with T2(SS) samples collected 3 to 5 h post-application. Maximum observed concentrations for these drugs in T2(SS) tile effluent were 1045, 4117 and 1040 ng L^{-1}, respectively. Given that there were no data on the concentrations of acidic drugs in the LMB, estimates of LMB concentrations were performed using maximum observed tile concentrations and mixing equations accounting for tile baseflow dilution effects, and with the assumption that all LMB-induced tile flow was composed exclusively of LMB. Using this method, the maximum estimated LMB concentrations for the acidic compounds, using data collected from all tiles, were 1835 ng L^{-1} for naproxen, 5863 ng L^{-1} for ibuprofen, and 1772 ng L^{-1} for gemfibrozil. For all tiles, these acidic drugs were present at concentrations below LOQ after JD 295. The T6(SS) had the maximum observed mass load (42,107 ng 15 min^{-1}) for acetaminophen, followed by T4(SS) (21,388 ng 15 min^{-1}). For acetaminophen, all observed tile water samples collected after 3–5 h post-application, were below the LOQ of 35.3 ng L^{-1}. The estimated LMB concentration of acetaminophen, as calculated above, was 4475 ng L^{-1}. For all the acidic drugs analyzed in samples from JD 294–295, tile mass loads were significantly higher for the SS treatment than the A treatment ($p<0.1$; *t*-test).

The sulfonamide antimicrobials (Fig. 4) were not detected at concentrations above the LOQ in any tile system >5 h post-application. In fact, for sulfapyridine, tile water concentrations at 3–5 h post-application in the T2(SS) samples were only marginally above the LOQ, with a maximum observed concentration of 22.4 ng L^{-1}. Tile water concentrations of sulfamethoxazole exceeded the LOQ for several tile systems up to 1 h post-application and up to 5 h for T2(SS); T2(SS) exhibited the maximum observed concentration of 322.8 ng L^{-1}. The average tile mass loads (ng 15 min^{-1}; JD 294–295) of sulfamethoxazole and sulfapyridine were significantly ($p<0.1$; *t*-tests) higher for the SS treatment than the A treatment . The only observation of fluoxetine exceeding the LOQ in tile water was for T2(SS), at 9 ng L^{-1} 3–5 h post-application. This drug could not be detected in any other tile system at any time.

The maximum concentrations of carbamazepine (1136 ng L^{-1}), cotinine (301 ng L^{-1}), and triclosan (3676 ng L^{-1}) were detected in T2(SS) approximately 3 h following application; whereas maximum concentrations for atenolol (267 ng L^{-1}) were observed for T4(SS) 1 h post-application (Fig. 5). The atenolol LMB concentration (Table 2) was somewhat lower than the maximum concentrations found in tile effluent. On average, the next highest PPCP concentrations were observed in the other SS plots. However, T5(A) was the only AerWay-treated tile system in which relatively high concentrations of carbamazepine, cotinine, and triclosan were observed. Concentrations of these PPCPs declined rapidly after JD 295, but could be observed above the LOQ during some discrete rain events post-application. Fig. 6 illustrates the impact of LMB land application practice on the mass loads of these PPCPs for JD 294 and 295. In fact, for this time period, these PPCP mass loads were significantly higher ($p<0.1$; *t*-test) for the SS treatment than the A treatment. However, for the remainder of the study season (JD > 295), triclosan mass loads were significantly higher ($p<0.1$) for the A treatment than the SS treatment, while atenolol mass loads were still significantly ($p<0.1$) higher for the SS than the A treatment.

Fig. 5 – Triclosan, carbamazepine, atenolol, and cotinine concentrations in tile water for application-induced tile discharge, and post-application tile discharge events.

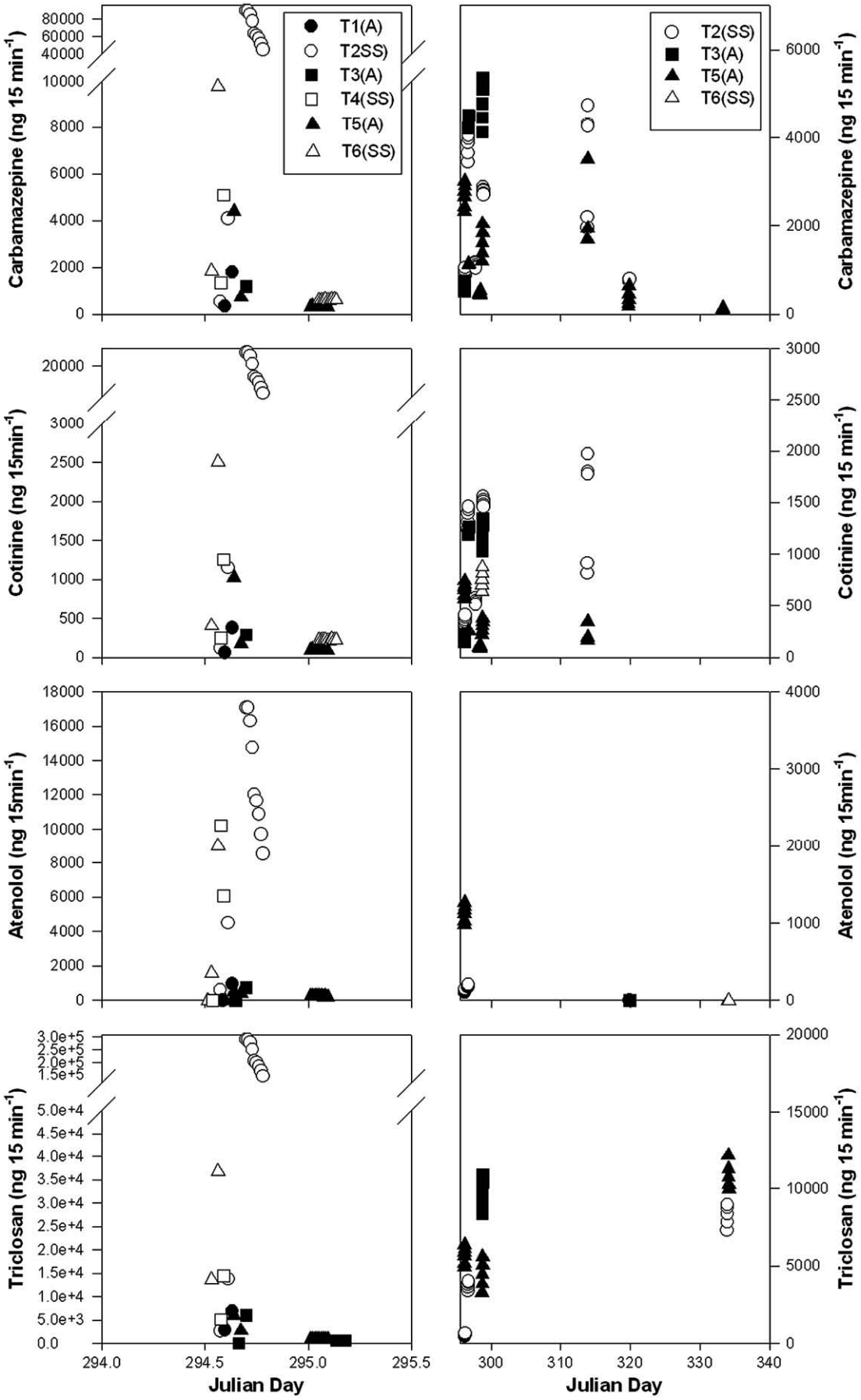

T1(A)
T2SS)
T3(A)
T4(SS)
T5(A)
T6(SS)
T2(SS)
T3(A)
T5(A)
T6(SS)
Carbamazepine (ng 15 min-1)
Cotinine (ng 15min-1)
Cotinine (ng 15 min-1)
Atenolol (ng 15min-1)
Triclosan (ng 15 min-1)
Julian Day
Julian Day

Table 4 – Linear regression equations used to predict tile PPCPs concentrations (Y, in ng L^{-1}) from concurrently measured tile RWT concentrations (x, in μ g L^{-1}) using all respective treatment tile data, the R^2 of the linear regression model, and the standard error of the estimate (ng L^{-1})

	Linear regression equation, R^2, standard error of estimate			
PPCPs	A JD 294	SS JD 294	A JD 295–340	SS JD 295–340
Carbamazepine	Y=9.48x, 0.93, 21.18*	Y=3.88x, 0.99, 16.22*	Y=2.85x, 0.92, 5.11*	Y=2.83x, 0.86, 4.37*
Atenolol	Y=2.20x, 0.54, 17.17*	Y=3.99x, 0.95, 16.86*	Y=1.68x, 0.75, 5.93*	Y=1.59x, 0.78, 3.30*
Cotinine	Y=2.32x, 0.95, 4.67*	Y=1.03x, 0.99, 4.00*	Y=0.82x, 0.88, 1.85*	Y=1.23x, 0.87, 1.83*
Sulfamethoxazole	Y=2.04x, 0.92, 4.97*	Y=1.12x, 0.99, 15.07*	Y=0.47x, 0.74, 1.67*	Y=1.00x, 0.66, 2.77*
Sulfapyridine	Y=0.43x, 0.96, 0.75*	Y=0.08x, 0.95, 2.02*	Y=0.08x, 0.81, 0.24*	Y=0.15x, 0.70, 0.38*
Triclosan	Y=15.37x, 0.87, 53.35*	Y=12.57x, 0.99, 86.71*	Y=6.13x, 0.83, 16.64*	Y=2.91x, 0.59, 9.29*
Acetaminophen	Y=20.15x, 0.92, 47.03*	Y=13.65x, 0.98, 34.46*	Y=0.56x, 0.14, 4.33	Y=0.003x, 0.02, 0.08
Naproxen	Y=7.77x, 0.92, 19.07*	Y=3.57x, 0.99, 9.95*	Y=0.75x, 0.14, 5.76	Y=1.24x, 0.53, 4.46*
Ibuprofen	Y=25.30x, 0.92, 59.94*	Y=14.05x, 0.99, 51.46*	Y=2.06x, 0.22, 12.16*	Y=6.93x, 0.59, 21.82*
Gemfibrozil	Y=7.57x, 0.92, 18.18*	Y=3.55x, 0.99, 7.41*	Y=1.31x, 0.15, 9.86*	Y=1.04x, 0.53, 3.76*

Regression models were generated for data collected on JD 294 (LMB application day), and for JD 295–340 (remainder of the study period).
* $=p<0.1$ level.

Table 4 indicates for JD 294–295 data (exclusively the LMB-induced tile hydrograph event), that RWT predicts well PPCPs concentrations in tile water for both treatments. Of all the PPCPs, atenolol had the weakest relationship with RWT. Overall, there were slightly smaller R^2 values and slightly higher standard errors of estimates for the A treatment, relative to the SS treatment. For the remainder of the study period (JD 296–340), R^2 values were generally lower than those for JD 294–295, but were still strong for most PPCPs, with the exception of the acidic drugs. Continuous RWT sensors were utilized to estimate study period mass loads (Table 5) of the various PPCPs in T3(A) and T6(SS) utilizing tile-specific linear regression functions. Table 5 shows that the coefficients of determination for T3(A) predicted vs. observed PPCPs concentrations were notably lower than those for T6(SS). The mass of each PPCP exported via tile drainage for the plots as a percentage of the total amount applied to the plots was generally higher for T6(SS) relative to T3(A).

4. Discussion

The PPCPs and RWT moved rapidly through the soil to the depth of tile drains, usually within minutes following land application, regardless of the application treatment. This is entirely consistent with the detection of other contaminants from biosolids, such as enteric bacteria, nitrogen, and phosphorus that were sampled concurrently in the same tile water samples (Lapen et al., 2008). It is assumed that these contaminants were transported rapidly by gravity-based flow through large pore networks in the soil; primarily worm burrows (Turpin et al., 2007; Ouellet et al., 2008) that directly intersect the subsurface drainage tile lines (Fig. 7). Burrow networks interacting with tile drains has been noted in other studies (Fleming and Bradshaw, 1992; Nuutinen and Butt, 2003). Transport of contaminants to tile was also facilitated by the fluidity of the LMB, which on the basis of total solids content, was likely near that of water (Malgeryd and Wetterberg, 1996). In that context, our results are probably representative of the contaminant transport potential of PPCPs carried in very dilute wastewaters such as those that are designated as reclaimed (Kinney et al., 2006b; Pedersen et al., 2005). Sorption of PPCPs to the walls of large and highly transmissive macropores at application is likely minimal in comparison to the mass moving to depth, especially given the rapid flow rates that existed in at least the largest contributing pore networks (Jensen et al., 1998). Gruber et al. (1990) also found that the leaching of the veterinary drug, avermectin increased as a result of preferential flow through cracks in a silt loam soil.

The AerWay SSD land application approach significantly reduced PPCP tile mass loads during the critical time period between application and the first post-application rain event, compared to the surface spread followed by incorporation method. The A treatment spreads material over the surface of soil immediately tilled by aerator-type tines. Such pre-tillage increases available porosity, lateral infiltrability, and sorptivity in the tillage layer, and also truncates large liquid transmitting pore networks at the surface (Turpin et al., 2007). For a conventional surface spread plus incorporation scenario, the incorporating tillage activity typically occurs hours after the application, which is far too late to reduce application-based macropore flow of contaminants to tile drainage and groundwater depths; at least for the macroporous type soils observed. In support of these findings, Kay et al. (2004) found when soils were disked prior to slurry application of animal waste, loss of veterinary antibiotics to tile drains was reduced.

The acidic drugs, fluoxetine, and the sulfonamides exceeded the LOQ in tile water only for the application-induced tile hydrograph event, and not during subsequent precipitation-induced tile flow events. On the other hand, cotinine, carbamazepine, triclosan, and atenolol were observed both at the time of application and during tile flow events that occurred later in the study period. The dissipation, biodegradation, and adsorption of each PPCP in the soil determines its availability for transport through the soil profile (Drillia et al., 2005); and these processes

Fig. 6 – Triclosan, carbamazepine, atenolol, and cotinine tile mass loads (ng 15 min^{-1}) for application-induced tile discharge, and post-application tile discharge events.

Table 5 – Linear regressions of predicted PPCPs concentrations (Y) in ng L^{-1} (as derived from predicting PPCPs from continuous RWT measurements at T3(A) and T6(SS)) vs. observed PPCPs concentrations (x = measured)

PPCPs and RWT	T3(A)			T6(SS)			Study period export (A:SS)
	Linear regression equation and (R^2)	Study period mass load (ng)	Study period PPCPs tile export as % of total applied[a]	Linear regression equation and (R^2)	Study period mass load (ng)	Study period PPCPs tile export as % of total applied	
Carbamazepine	Y = 0.86x (0.73)	533,768	2.8	Y = 0.99x (0.98)	449,209	2.4	1.17
Atenolol	Y = 0.83x (0.84)	8841	0.8	Y = 0.95x (0.94)	161,298	13.7	0.06
Cotinine	Y = 0.73x (0.37)	59,846	2.0	Y = 0.97x (0.96)	122,390	4.0	0.5
Sulfamethoxazole	Y = 0.73x (0.62)	168,845	28.5	Y = 0.99x (0.99)	203,232	34.3	0.83
Triclosan	Y = 0.77x (0.65)	839,186	3.1	Y = 0.91x (0.90)	956,255	3.5	0.89
Acetaminophen	Y = 0.80x (0.77)	88,978	0.3	Y = 0.99x (0.99)	691,998	2.2	0.14
Naproxen	Y = 0.72x (0.21)	8831	0.07	Y = 0.99x (0.99)	144,203	1.1	0.06
Ibuprofen	Y = 0.72x (0.21)	52,962	0.1	Y = 0.99x (0.99)	569,736	1.4	0.07
Gemfibrozil	Y = 0.72x (0.21)	10,865	0.09	Y = 0.98x (0.97)	168,459	1.3	0.07
Rhodamine WT	NA	614,663	1.0	NA	327,229	0.5	2.00

a, for acidic drugs % based on estimated maximum concentrations determined from tile flow measurements, NA = not applicable.
R^2 is given in parenthesis. Total mass loads of PPCPs and RWT in (ng) for study period (application to JD 294–340), study period mass loads as a percent of total amount of PPCPs applied to plot, and ratios of A and SS study period PPCPs mass loads are also presented.

are dependent on many site-specific conditions such as soil oxygen status (Ying et al., 2007), soil temperature, pH, organic content (Topp et al., 1997; ter Laak et al., 2006), and the characteristics of the matrix carrying the PPCPs (Rogers, 1996; Boyd et al., 2003; Jones et al., 2005). Carbamazepine and triclosan, which were detected in tile drainage up to several weeks after the application, are relatively persistent in environmental matrices and during wastewater treatment (Ferrari et al., 2003; Miao et al., 2005; Halden and Paull, 2005; Kinney et al., 2006a). Carbamazepine has a low leaching potential based on its adsorption characteristics with soil, but has been detected in groundwater (Sacher et al., 2001; Heberer, 2002; Williams et al., 2006). Triclosan partitions preferentially into wastewater organic material (Heidler et al., 2006) and dissipates slowly in soil (Ying et al., 2007), whereas cotinine is readily biodegradable in environmental matrices (Bradley et al., 2007). In our study, cotinine only exceeded LOQ once >10 days post-application. Maurer et al. (2007) found that atenolol has a half life of a few hours during sewage treatment, but Bendz et al. (2005) found atenolol and other β-blockers to be environmentally persistent. In this study, tile mass loads of one of the more persistent compounds, ttriclosan, were found, for time periods following the LMB-induced tile hydrograph event, to be greater for A relative to SS (as per RWT). Presumably, AerWay tillage activity augmented PPCP sequestration in the tillage layers, and during post-application rain events, persistent PPCPs stored in the tillage layer were re-mobilized to tile drain systems to a degree significantly greater than that which occurred for SS where absolute PPCP storage in surface soils was likely smaller.

Interestingly, fluoxetine was detected in the 300 ng L^{-1} range in the raw LMB, yet it was not detected above LOQ for any tile flow event. Nevertheless, fluoxetine has been shown to be persistent in the environment (Kolpin et al., 2002; Kinney et al., 2006a), relatively recalcitrant to hydrolysis, photolysis, and microbial degradation and readily sorbed to sediment, where it can be persistent (Kwon and Arbrust, 2006). While fluoxetine may have been gravity-driven to depth rapidly during application, it may have readily bound to soil and sediments and subsequently been sequestered or transformed.

Although the estimated acidic drug concentrations in LMB exceeded 1000 ng L^{-1}, they were only detected in the application-induced tile hydrograph event. Concentrations of acidic drugs did not exceed the LOQ in tile water during subsequent observations, suggesting that the acidics were labile or were bound to soil. Significant sorption and microbial degradation of ibuprofen reduced leaching potential (Oppel et al., 2004), and acetaminophen was found to accumulate in soils treated with wastewater, despite its high solubility (Kinney et al., 2006b).

In order to assess the relative PPCP loading risk in tile effluent for weeks following application, RWT was used as a tracer to predict mass loads of PPCPs in the tile discharge system. Relationships between RWT and PPCPs concentrations for the application-induced hydrograph event were very good, despite the slightly better predictions for the SS treatment relative to the A treatment. These overall high linear regression R^2 values were

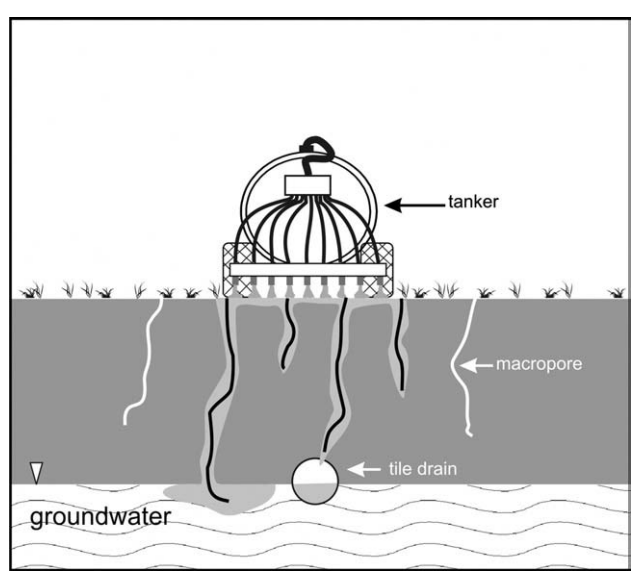


Fig. 7 – Conceptualization of typical land application of LMB, and nature of land application-induced contamination of tile drainage systems and groundwater.

a result of the rapid gravity-based transport of LMB to the tile drains through large interconnected pores that minimized contact with soil, which reduced mass sorption (Jensen et al., 1998). Following application, the relationship between the concentrations of RWT and the various PPCPs varied significantly from very good to poor. This was presumably due to differences in dissipation and sorptive characteristics between RWT and each PPCP. The AerWay pre-tillage method reduced soil macropore contributions to tiles and therefore augmented LMB liquid, PPCP, and RWT sorption and storage in the tilled surface layers. Under these circumstances, the strength of the RWT and PPCPs linear relationships were weaker. Subsequent to the application event, the RWT- PPCPs linear relationship strength decreased, but remained nevertheless strong to modest. Greater parity in the R^2 values between the A and SS treatment post-application supports the contention that tillage impacted variably PPCPs vs. RWT linear relationships, since post-application rain events would have interacted with tilled surface soils for both treatments. This study showed that RWT is potentially a robust tracer that mimics the transport and mass loadings of many PPCPs over timeframes of weeks. However in this study, we did not characterize RWT sorption (Edwards et al., submitted for publication) and dissipation kinetics in soil, but in these experiments, photolysis was likely minimal (Tai and Rathbun, 1988). Nevertheless, there must be considerations of the limitations of optical sensing RWT in samples significantly influenced by biosolid materials (Edwards et al., submitted for publication).

Some of the PPCP concentrations in tile drainage water were high enough to be of concern with respect to biological impact. For instance, triclosan was detected at 3676 ng L^{-1} shortly after application. Frogs (*Rana catesbeiana*) exposed to 150 ng L^{-1} triclosan for several days showed altered thyroid hormone-mediated gene expression and development (Veldhoen et al. 2006). But this study was conducted to represent a 'worst' case scenario in terms of contamination risk to tiles. Namely: i) selected PPCPs were spiked into LMB, ii) the LMB was capable of readily moving into a porous medium, unlike dewatered material, iii) the soil was notably macroporous in terms of liquid-transmitting worm burrows, iv) the fall application season was wet, with frequent and heavy rainfall, and v) the tiles were continuously flowing over the course of the study period. In addition, the soil temperature for the study period averaged 8 °C (range = 5–12 °C) at the 60 cm depth and 5 °C (range = −1–10 °C) at the 10 cm depth, and soil oxygen concentrations have been found at this particular study site to be low (<0.02 kg O_2 m^{-3} of soil) (Lapen et al., 2004). These soil conditions could have augmented PPCP persistence, relative to warmer and more oxygen-rich settings (Topp et al., 1997; Ying et al., 2007). However, the overall PPCP tile loadings determined via the RWT vs. PPCP regressions were not exceedingly large, ranging between 8831 and 956,255 ng over a 40 day study period. For other weather/soil scenarios, such as might be expected during drier conditions in spring or early summer, the tile mass loads of PPCPs would likely be even lower.

Overall, these results provide a framework for estimating loadings of PPCPs in tile drainage systems from land application of LMB, a common farming practice in the province of Ontario, Canada. The significance of this practice can now be contrasted with other routes of environmental exposure to PPCPs, such as sewage outflows, and land application of other types of wastewaters and dewatered materials. But PPCP monitoring was only conducted over a relatively short period of time, and persistent PPCPs adsorbed to soil or concentrated in groundwater, may manifest in tile effluent at times surpassing the termination of monitoring in this experiment.

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