Chemosphere 87 (2012) 194–203

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Pharmaceutical and personal care products in groundwater, subsurface drainage, soil, and wheat grain, following a high single application of municipal biosolids to a field

N. Gottschall [a], E. Topp [b], C. Metcalfe [c], M. Edwards [a], M. Payne [d], S. Kleywegt [e], P. Russell [a], D.R. Lapen [a,*]

[a] Agriculture and Agri-Food Canada, Ottawa, ON, Canada K1A 0C6
[b] Agriculture and Agri-Food Canada, London, ON, Canada N5V 4T3
[c] Water Quality Centre, Trent University, Peterborough, ON, Canada K9J 7B8
[d] Ontario Ministry of Agriculture, Food and Rural Affairs, Stratford, ON, Canada N5A 5T8
[e] Ontario Ministry of the Environment, Toronto, ON, Canada M4V 1M2

ARTICLE INFO

Article history:
Received 5 July 2011
Received in revised form 6 December 2011
Accepted 8 December 2011
Available online 31 January 2012

Keywords:
Pharmaceuticals
Municipal biosolids
Land application
Groundwater
Soil
Crop

ABSTRACT

Dewatered municipal biosolids (DMBs) were applied to a field at a rate of ~22 Mg dw ha^{-1} in October 2008. Pharmaceuticals and personal care products (PPCPs) were monitored in groundwater, tile drainage, soil, DMB aggregates incorporated into the soil post-land application, and in the grain of wheat grown on the field for a period of ~1 year following application. Over 80 PPCPs were analyzed in the source DMB. PPCPs selected for in-depth monitoring included: antibiotics (tetracyclines, fluoroquinolones), bacteriocides (triclosan, triclocarban), beta-blockers (atenolol, propranolol, metaprolol), antidepressants (fluoxetine, citalopram, venlafaxine, sertraline), antifungals (miconazole), analgesics (acetaminophen, ibuprofen) and anticonvulsants (carbamazepine). PPCPs in tile were observed twice, ~3 weeks and 2 months post-application. Of all PPCPs measured in tile drainage, only carbamazepine, ibuprofen, acetaminophen, triclosan, triclocarban, venlafaxine, and citalopram were detected (5–74 ng L^{-1}). PPCPs were not detected in groundwater >2 m depth below the soil surface, and concentrations above detection limits at 2 m depth were only observed once just after the first rain event post-application. In groundwater, all compounds found in tile, except carbamazepine, acetaminophen and citalopram, were detected (10–19 ng L^{-1}). PPCPs were detected in DMB aggregates incorporated in soil up to 1 year post-application, with miconazole and fluoxetine having the lowest percent reductions over 1 year (~50%). For several compounds in these aggregates, concentration declines were of exponential decay form. No PPCPs were detected in the grain of wheat planted post-application on the field. No PPCPs were ever detected in water, soil or grain samples from the reference plot, where no DMB was applied.

Crown Copyright © 2012 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Pharmaceutical and personal care products (PPCPs) include compounds such as antibiotics, antifungals, antidepressants, bacteriocides, and various other medications which can become part of the wastewater stream. The wastewater treatment process does not fully eliminate PPCPs from final effluent, and PPCPs can accumulate in sewage sludge, or biosolids (Lishman et al., 2006; Spongberg and Witter, 2008; Onesios et al., 2009). The ever-increasing use (and subsequent disposal) of PPCPs has been cause for concern in recent years, given that they are now commonly detected in surface and groundwater (Halling-Sorensen et al., 1998; Ellis, 2006; Musolff et al., 2009; Metcalfe et al., 2010), and, moreover, their long-term ecotoxicity potential is not well understood (Jjemba, 2006). Hence, there is general concern over the impact of PPCPs in the environment, and as such routes of exposure and environmental concentrations need to be elucidated.

In agriculture, municipal biosolids can be a source of nutrients and organic matter for crop growth. In many countries and jurisdictions, land application of biosolids is routinely employed. A wide range of contaminants of emerging concern, including PPCPs have been detected in biosolids destined for land application (Xia et al., 2005; Kinney et al., 2006b). In our previous studies, we detected PPCP residuals resulting from land application of municipal biosolids to agricultural field soils in groundwater and subsurface drainage networks (tile) (Lapen et al., 2008; Edwards et al., 2009), as well as in artificially produced surface runoff (Topp et al., 2008b; Sabourin et al., 2009). As a result of these types of transport pathways, some PPCPs have potential to reach concentrations in receiving waters that can pose an environmental concern (Langdon et al.,

* Corresponding author. Tel.: +1 613 759 1537; fax: +1 613 759 1701.
E-mail addresses: david.lapen@agr.gc.ca, natalie.gottschall@agr.gc.ca (D.R. Lapen).

0045-6535/$ - see front matter Crown Copyright © 2012 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2011.12.018

2010). Many PPCPs can dissipate quickly after being applied to soil, like naproxen, yet others, such as triclosan and fluoroquinolones, have been shown to be more persistent in the soil–water environment (Golet et al., 2003; Ying et al., 2007; Topp et al., 2008a; Lozano et al., 2010). From an agricultural perspective, it is also critical to understand the potential for plant (crop) uptake of PPCPs resulting from land application of biosolids, since PPCPs have been shown to be absorbed and translocated into above-ground tissues (Boxall et al., 2006; Wu et al., 2010).

In the province of Ontario, Canada, the maximum allowable amount of municipal biosolids that can be applied per 5 years is 22 Mg dw ha^{-1} (Ministry of the Environment, 2011). Lapen et al. (2008) found that a single land application of liquid municipal biosolids (LMB) applied at a rate of ~1 Mg dw ha^{-1} (93, 500 L ha^{-1} as a total application rate including solids and water) could travel rapidly to subsurface drainage networks (tile) and shallow groundwater (~1 m depth below surface). Edwards et al. (2009) found that precipitation shortly after land application of dewatered municipal biosolids (DMBs), applied at a rate of ~8 Mg dw ha^{-1}, could facilitate leaching of PPCPs to subsurface drainage systems (~0.8 m depth below surface). Yet the soils examined in those studies had a high degree of vertical macroporosity (Larsbo et al., 2009) that facilitated rapid preferential flow of PPCPs to depth in the soil. We previously showed that soil characteristics (Larsbo et al., 2009), weather, the form of the biosolids (i.e. LMB, DMB) (Edwards et al., 2009), and land application approach (Lapen et al., 2008) can impact the degree of PPCP transport to important ground and surface water receptors. Thus, field-scale studies that assess environmental concentrations or loading need to be carried out on different soil-management systems in order to help validate predicted environmental concentrations and risks (Metcalfe et al., 2009), elucidate dominant exposure pathways, and characterize dissipation kinetics (O'Connor et al., 2005; Agyin-Birikorang et al., 2010).

This study, conducted at a field scale, assessed the potential for PPCPs in land applied DMB to contaminate groundwater and subsurface artificial drainage networks that can rapidly export field drainage waters to the broader surface water environment. In addition, since PPCPs that persist in DMB biosolid aggregates in the soil could serve as a potential reservoir for PPCP contamination over the long term (Xia et al., 2005), we examined the dissipation of PPCPs in biosolid aggregates incorporated in the soil following application. Also we examined PPCP uptake in wheat (*Triticum* spp.) grain produced on these same field soils. The DMB in this study was applied at a single application rate that was ~3 times higher than that of the Edwards et al. (2009) study: at the current maximum regulatory application rate in the province of Ontario (Ministry of the Environment, 2011). Thus, findings in this study provide measured PPCP concentrations in field scale water, soil, and crop systems where relatively 'high' amounts of biosolids are applied to land in a single application.

2. Materials and methods

2.1. Study site description

The study site is located on a 14 ha experimental agricultural field located on Agriculture and Agri-Food Canada experimental research station lands in Ottawa, Ontario Canada. The climate in the region is humid continental. Average monthly temperatures range between −10.8 and 20.9 °C and total annual rainfall averages 732 mm (Environment Canada, 2011). As illustrated in Fig. 1, the field was subdivided into four distinct field sections of approximately 3 ha each. Field sections 1 and 4 are the only sections relevant for this study, as they represent the biosolid application plot and the reference plot (i.e. no biosolid application), respectively. Surface soils across the western portion of both field sections are generally more silty and clayey than the eastern portion of the field; in addition, surface soils in field section 1 are generally finer in particle size than in field section 4 (Fig. 1, Table 1). Both field sections 1 and 4 are independently tile drained, with a lateral tile spacing of 15 m. Maximum tile drain depth is ~1.1–1.2 m below the soil surface near headers. The field has been used to grow primarily corn (*Zea mays* L. spp.), soybean (*Glycine max.*), and wheat since 2003. During the 2008 summer season, the field was kept fallow, outside of one very light surface tillage and two treatments of glyphosate (early July and September) imposed for weed control purposes. Biosolids were never applied on this field prior to the study.

2.2. DMB application, soil incorporation, and planting

The DMB used for this application was obtained from the city of Ottawa's wastewater treatment plant (Robert O. Pickard Environmental Centre); the biosolids were anaerobically digested and then dewatered by centrifuge to make the final product. The DMB was applied at a rate of 22 Mg dw ha^{-1} to field section 1 using a Samson Flex 20 spreader (Samson Agro A/S, Denmark). This application rate is currently the maximum allowed provincial rate, which is 3 times the application rates employed in our previous study described by Edwards et al. (2009; Ministry of the Environment, 2011). Land application occurred in autumn on day of year 277 (October 3, 2008). Within 24 h post-application, DMB was incorporated into soils, as per provincial regulations (Ministry of the Environment, 2011), to a depth of ~0.2 m by mouldboard plowing. Mouldboard plowing folds the surface soil over onto itself so that the original soil surface is typically at plow depth in the soil. About 3 d post-application (DPA), winter wheat (Pioneer, soft red winter wheat 25R47) was planted following seed bed cultivation with a mulch finisher. However, due to extremely poor winter wheat growth on the field, spring wheat (Sable, hard red spring wheat) was planted on April 30, 2009. Table 2 shows the basic physical and chemical characteristics of the DMB, including some select PPCPs that had notably higher relative concentrations.

2.3. Sample collection

2.3.1. Groundwater monitoring

Each field section had two piezometer nests/wells (Fig. 1). The wells and piezometers were composed of PVC pipe. The piezometers had slotted intake lengths of 0.14 m. Sand was packed from the bottom of the piezometer to 0.3 m above the top of the slotted intake on the pipe. Bentonite was used to seal the piezometers from the sand pack to the soil surface. Each piezometer nest was composed of three piezometers with intakes centered at 2, 4 and 6 m below the soil surface. Nests were located midway between the tile drain laterals that ran in roughly an east–west manner along each field section. Water was collected from the piezometers for analysis of PPCPs using a peristaltic pump (Masterflex E/S portable sampler) before and after DMB application. Teflon tubing inserted down the length of the piezometer at sample time was used to sample the water; tubing was rinsed with distilled water between samples. All piezometers were fully pumped of water and allowed to recover prior to water sampling. Sampling took place as soon as piezometer water levels recovered to pre-pump levels (typically within a 24 h period). For each field section, water from each piezometer representing a particular depth was pooled for PPCP analysis (e.g., all 2 m piezometers for field section 1 were pooled at sampling time). Groundwater was sampled on a monthly basis pre- and post-application, with additional sampling following

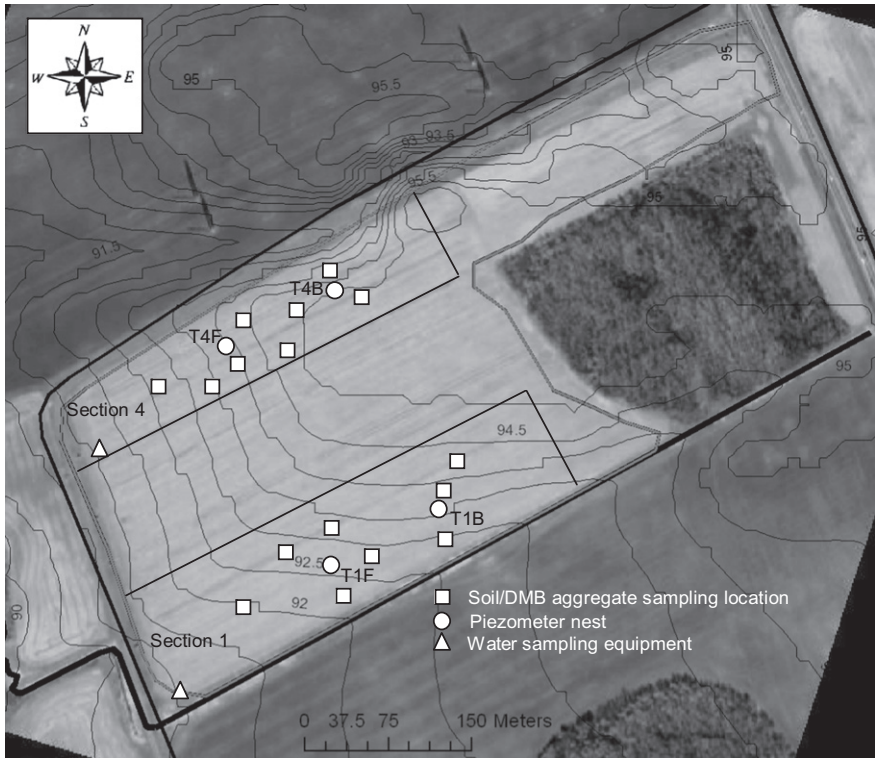

Fig. 1. Map of study site showing topography (contour intervals are in m), locations of tile water sampling equipment, piezometer nests, and soil/DMB aggregate sampling locations.

Table 1
Key soil characteristics of study site; CEC = cation exchange capacity, OC = organic carbon, BD = bulk density. Soil particle size was determined via hydrometer methods, and soil pH was determined using a 1:1 soil:water ratio. Soil was collected from cores taken near piezometer nests at each field section. Locations are indicated on Fig. 1. –, Not determined.

Location	Depth (m)	CEC (meq 100 g^{-1})	% Sand	% Silt	% Clay	% OC	pH	BD (g cm^{-3})
Section 1 (T1B)	0–0.3	20	44	36	20	0.84	5.7	1.4
	0.3–0.6	21	46	26	28	0.28	–	1.4
	0.6–0.9	16	52	27	21	0.24	7.3	1.4
Section 1 (T1F)	0–0.3	23	45	39	16	1.41	5.3	1.6
	0.3–0.6	25	39	19	42	0.27	6	1.5
	0.6–0.9	20	31	17	52	0.19	6.7	1.5
	0.9–1.4	–	33	30	37	0.13	–	–
	1.4–2	15	24	34	42	0.1	7.2	–
	2–3	15	17	34	49	0.14	7.4	–
	3–4	29	32	39	28	0.12	–	–
Section 4 (T4B)	0–0.3	11	75	19	6	0.78	6.1	1.5
	0.3–0.6	6	74	16	10	0.21	7	1.5
	0.6–0.9	13	44	30	26	0.16	6.9	1.4
Section 4 (T4F)	0–0.3	14	60	32	8	0.7	5.9	1.5
	0.3–0.6	14	41	29	30	0.28	6.8	1.6
	0.6–0.9	15	35	32	33	0.15	6.8	1.5
	0.9–1.4	14	32	34	34	0.11	6.8	–
	1.4–2	12	31	35	34	0.14	–	–
	2–3	16	26	32	42	0.1	–	–
	3–4	14	26	43	30	0.18	7.1	–

rain events that stimulated tile flow. A total of 9 ground water sampling times were selected for PPCP analysis.

2.3.2. Tile water (subsurface drainage)

In-line water flow control structures (Agri Drain Corp.; Adair, Iowa) were installed on the tile drain headers for each field section at the water sampling equipment locations (Fig. 1). V-notch weirs (angle of 30.5°) were installed in the bottom of the structures (there was no water flow control imposed) in order to rate discharge. Water level at each weir was measured via bubblers (ISCO bubbler module 730; Lincoln, Nebraska). ISCO 6712 automated water samplers with Teflon water intake tubing fixed behind the weirs were used to sample tile drainage water for PPCP analysis. Water was sampled in 1 L Teflon lined ISCO bottles, as described previously by Lapen et al. (2008). Sampling was set to trigger at specified bubbler depths at the initiation of drainage, or an increase in water level at the weir, but trigger thresholds were adjusted depending on weather and antecedent soil water

Table 2
Physical and chemical properties of the dewatered municipal biosolids (DMBs) used in this study. Concentrations are on a dry weight basis.

Parameter	Concentration (detection limit)
Total Kjeldahl Nitrogen (mg g^{-1})	31 (0.1)
Total Phosphorous (mg g^{-1})	41 (0.1)
Total coliforms (cts g^{-1})	1980000 (0)
Escherichia coli (cts g^{-1})	992000 (0)
Faecal streptococcus (cts g^{-1})	105000 (0)
Clostridium perfringens (cts g^{-1})	9400000 (0)
pH	7.9
Moisture (%)	74.8 (0.1)
Electrical conductivity (mS cm^{-1})	4.4 (0.01)
Organic carbon (%)	23.5 (0.01)
NO_3–N (μg g^{-1})	6 (1)
NH_3–N (μg g^{-1})	18200 (100)
PPCPs (ng g^{-1})	
Anticonvulsants	
Carbamazepine	183 (3)
Analgesics	
Ibuprofen	64 (10)
Fluoxetine	109 (3)
Citalopram	114 (3)
Beta-blockers	
Metoprolol	108 (4)
Propranolol	119 (4)
Antibiotics	
4-Epitetracylcine	334 (12)
Tetracycline	513 (12)
Azithromycin	228 (3)
Ciprofloxacin	3260 (12)
Norfloxacin	1010 (30)
Ofloxacin	1400 (3)
Bacteriocides	
Triclocarban	4940 (6)
Triclosan	10900 (120)
Antifungals	
Miconazole	341 (3)
Antihistamines	
Diphenhydramine	689 (1.2)

Note: Only selected pharmaceuticals were included in this table. Please see Table S1 for a complete list of PPCPs analyzed in solids and water, and the Materials and Methods section for PPCP detection limit definitions.

conditions in order to sample important tile drainage hydrograph times. Briefly, tile water was sampled along tile drain hydrographs (typically heavier front-end sampling starting at 15 min post-trigger, to capture the rising front of the hydrograph, followed by additional sampling at 1, 2 and 6 h intervals, to capture the peak and then recession limb) pre- and post-application. Only 1 sample per tile sampling event was analyzed for PPCPs for each field section, and this sample was selected based on flow conditions, typically targeting the peak flow period. Sampling was also conducted during very low tile flow conditions. A total of 10 tile hydrograph events were selected for PPCP analysis over the study period. Water samples were frozen at −20 °C if they could not be analyzed immediately.

2.3.3. Sampling soil and incorporated DMB aggregates

DMB samples were taken on the day of application by collecting an equal volume (~500 cm^3) DMB subsample (representing bottom, middle, and top of each truck load) from each biosolid load applied to field. These sub samples were then mixed in a large bucket for 20 min to ensure homogeneity of the final composite sample, which was analyzed for biosolid constituents immediately.

Soil cores (0–0.3 m depth; 0.045 m diameter corer) were taken at multiple sampling times (pre-application, ~6 months post-application, and ~1 year post-application) from sampling locations on field sections 1 and 4 (Fig. 1). All cores taken for each field section at each sampling time were mixed for 20 min in Teflon bags to create 1 composite soil sample for that field section and time period. The samples were all taken within the immediate vicinity (within approximately 1 m) of the flagged soil sampling sites shown in Fig. 1. If samples could not be analyzed immediately, they were frozen at −20 °C until analysis.

Direct sampling of DMB aggregates that were incorporated (via the mouldboard plowing) in the soil at flagged soil/DMB aggregate sampling sites (Fig. 1) was possible because the mouldboard plowing technique (a commonly utilized fall tillage approach) used to incorporate the material limited mixing of DMB aggregates above tillage depth, thus allowing for identification of DMB aggregates in soil at ~0.2 m below surface for relatively longer periods of time. Small soil pits were excavated at each sampling time within roughly a meter of each flagged sampling site (Fig. 1), and samples of the incorporated DMB aggregates (which were recognizable in the soil even a year post-application) were carefully sampled at ~1 month, ~2 months, ~6 months and ~1 year post-application. DMB aggregates in soil ranged in size from ~2 to 5 cm^3 directly post-application, and decreased in size over time to <2 cm^3 by ~1 year post-application. It was ensured via weighing samples, that sample amounts from each DMB aggregate sample site were consistent in terms of bulk mass. All DMB aggregate samples from each field section for each time period were pooled, mixed in Teflon bags for 20 min to augment homogeneity of the composite sample, and frozen at −20 °C prior to analysis if samples could not be immediately processed.

2.3.4. Crop grain sampling

Wheat grain was sampled during harvesting on September 14, 2009. For each field section, samples were taken from the harvester grain storage bin at various intervals of travel along each respective field section. The reference field section was harvested prior to the biosolids field section to preclude cross-contamination. Interval-based samples, collected for each field section were of equal amounts by volume, and pooled, mixed, and immediately analyzed.

2.4. PPCP analyses

Pharmaceutical and personal care product analyses for water, land applied DMB, incorporated DMB aggregates, soil samples, and grain were carried out by AXYS Analytical Services Ltd. (ISO 17025) and/or the Water Quality Centre at Trent University. AXYS used method MLA-075, which is based on EPA method 1694 for analysis of pharmaceuticals (USEPA, 2007). The EPA 1694 method was modified by AXYS to include extra labelled internal standards and additional target analytes. Yet for the MLA-075 method, all EPA 1694 method QA/QC protocols and specifications were applied, including surrogate and recovery standards and use of blanks. Detection limits were calculated using the lowest calibration standard and adjusting for sample size and extract volume; the lower method calibration limit. A sample specific detection limit was also calculated for each sample run, to account for matrix interferences. The sample detection limit, defined as the concentration equivalent to 3 times the noise signal, was reported when it was larger than the lower method calibration limit. The Water Quality Centre followed methods described in Edwards et al. (2009), Metcalfe et al. (2010) and Scheurer et al. (2010), including using surrogate and recovery standards as well as blanks as part of QA/QC protocols. To calculate detection limits, standards were spiked into the appropriate matrix (water or biosolid) to a level that would produce a signal <10 times the baseline noise; detection limits were defined as 3 times the standard deviation of the signal produced. Briefly, for DMB samples analyzed for tetracycline and macrolide antibiotics, fluoroquinolones, antifungals, antihistamines, bacteriocides, anticonvulsants and nicotine metabolites,

extractions were conducted at AXYS by sonication with aqueous buffered acetonitrile and pure acetonitrile. Extracts were then cleaned-up by solid phase extraction, filtered and analyzed by LC/ESI-MS/MS. For analgesics, lipid regulators, antidepressants, and beta-blockers in DMB samples, extractions were carried out at the Water Quality Centre using pressurized liquid extraction, and then extracts were analyzed by LC/ESI-MS/MS. All soil samples were analyzed at AXYS following methods used to analyze DMB samples.

Tile water and groundwater samples were also analyzed at AXYS and the Water Quality Centre. Again, AXYS followed a modified EPA 1694 method, as for solids, and the Water Quality Centre followed methods described in Edwards et al. (2009), Metcalfe et al. (2010) and Scheurer et al. (2010). AXYS analyzed the same compounds as for solids, except for bacteriocides, anticonvulsants and nicotine metabolites, which were analyzed by the Water Quality Centre in addition to analgesics, lipid regulators, and antidepressants. Aqueous samples were first filtered and then the filtrate was cleaned up by solid phase extraction before analysis by LC/ESI-MS/MS. Prior to extraction and clean-up, all samples (solid and liquid) were adjusted to the required extraction pH and spiked with surrogates. Grain samples were processed and analyzed by AXYS in the same manner as other solid samples described above, following a modified EPA 1694. Table S1 provides a complete list of compounds analyzed in solid and liquid samples, as well as expected detection limits.

2.5. Soil monitoring and weather

Volumetric water content was measured throughout the study period pre- and post-application using a ESI Environmental Sensors Inc. (Environmental Sensors Inc., Victoria, British Columbia, Canada) MP917 with single-diode probes. Thermocouple based soil temperature and meteorological information were collected every half hour at the site throughout the study period. These data were logged with a Campbell Scientific Inc. (Campbell Scientific Inc., North Logan, Utah, USA) CR10 Datalogger and AM32 Relay Multiplexer. A Texas Electronics Inc. (Texas Electronics Inc., Dallas, Texas, USA) model TR-525 Rainfall Sensor was connected to the CR10 logger to monitor rainfall.

3. Results

3.1. General soil and weather information

The monitoring period post-DMB application was from October 3, 2008 to November 12, 2009. Total rain precipitation during this time period was 1070 mm (Fig. 2). Snow precipitation was 189.2 cm. Soil water content and soil temperature measured at 0.25 m depth in the soil at the study site are also shown in Fig. 2 over the duration of the study period.

3.2. Initial DMB PPCP concentrations

The DMB that was land applied was analyzed for more than 80 PPCPs representing a wide variety of compound classes. A comprehensive list of target compound concentrations in the DMB is given in Table S1 in the appendix. A large number of these PPCPs were either not detectable, or had very low concentrations in the DMB. A small suite of model PPCPs representing different compound classes were selected from the PPCPs analyzed in Table S1 for more detailed analyses in this paper (See Table S1). Most of these selected PPCPs were present in DMB at generally higher concentrations (>100 ng g^{-1} dw) relative to the other PPCPs. Overall, the fluoroquinolone antibiotics ofloxacin, ciprofloxacin, and norfloxacin, and the bacteriocide personal care products, triclosan and triclocarban, were present in DMB at the highest concentrations of all PPCPs measured (Table 2).

3.3. PPCPs in soil and DMB aggregates incorporated in the soil

None of the selected PPCPs were found above detection limits in soil cores (0–0.3 m depth) taken pre-application on field section 1. Within ~6 months post-application (194 DPA), only miconazole (5 ng g^{-1}), triclocarban (44 ng g^{-1}) and triclosan (98 ng g^{-1}) were detected in the soil. Just over 1 year post-application (405 DPA), only miconazole (127 ng g^{-1}), triclocarban (22 ng g^{-1}) carbamazepine (30 ng g^{-1}) and 2-hydroxy-ibuprofen (174 ng g^{-1}), a metabolite of ibuprofen, were detected. Due to analytical difficulties related to matrix interferences, there were no quantifiable results for fluoroquinolone antibiotics (ofloxacin, norfloxacin, ciprofloxacin) in soil cores. However, quantitative analysis of ofloxacin indicated that this antibiotic was, at least, 'present' in soil cores taken at 194 and 405 DPA.

For DMB aggregates incorporated in the soil sampled post-application, the antidepressants venlafaxine, sertraline and citalopram, as well as the beta-blockers atenolol, metoprolol and propranolol were not measured after 2 months post-application, and therefore, longer-term changes in the concentrations of these PPCPs could not be determined (Fig. 3). Sampled aggregates were around 2–5 cm^3 soon after application, and <2 cm^3 1 year post-application; albeit there was a high degree of variability. Concentrations of PPCPs generally declined over time in an exponential decay manner. Within ~6 months post-application, cotinine, acetaminophen, gemfibrozil and ibuprofen were undetectable in incorporated DMB aggregates, while the remaining compounds experienced concentration reductions of between 12% (ciprofloxacin) and 88% (carbamazepine) relative to the original DMB concentrations. By ~1 year post-application, fluoxetine and the antifungal compound, miconazole had the lowest percent reductions overall, at just over 50%, while the fluoroquinolones (ciprofloxacin, norfloxacin, and ofloxacin) had the lowest percent reductions as a group, ranging from 60% to 70%. At ~1 year post-application, most PPCPs were still detected, with the bacteriocides triclosan (1750 ng g^{-1}) and triclocarban (3100 ng g^{-1}) having the highest concentrations, followed closely by the fluoroquinolones (382–1310 ng g^{-1}). For most PPCPs in DMB aggregates incorporated in the soil, the declines in concentration fit a first-order exponential decay model (Table 3). The remaining compounds monitored in DMB aggregates (cotinine, ciprofloxacin, tetracycline, fluoxetine, diphenhydramine, and triclocarban), did not fit a first-order model at the $p = 0.05$ level. Since only parent compounds were monitored, the model represents a combination of decay and transformations, as well as leaching/mobilization into the soil profile (i.e., bulk dissipation). The PPCPs with the lowest k (decay rate constant, d^{-1}) values were miconazole ($k = 0.002$) and norfloxacin ($k = 0.0024$). The drug with the highest k value was ibuprofen ($k = 0.058$).

3.4. Tile and groundwater PPCP concentrations

None of the selected PPCPs examined in this study (see all the selected compounds in Table S1) were detected in tile drainage from either field section prior to DMB application. Following the first rain event to induce tile flow on October 25, 2008 (22 DPA), carbamazepine, acetaminophen, ibuprofen, triclosan, triclocarban, O-desmethyl venlafaxine (venlafaxine metabolite), venlafaxine, and citalopram were detected in tile drainage from field section 1 (Table 4a). Aside from carbamazepine, (detected again at 5 ng L^{-1} ~ 2 months post-application) no other PPCPs were detected after this first rain event post-application in tile water samples. The PPCP mass loads (tile discharge × sample

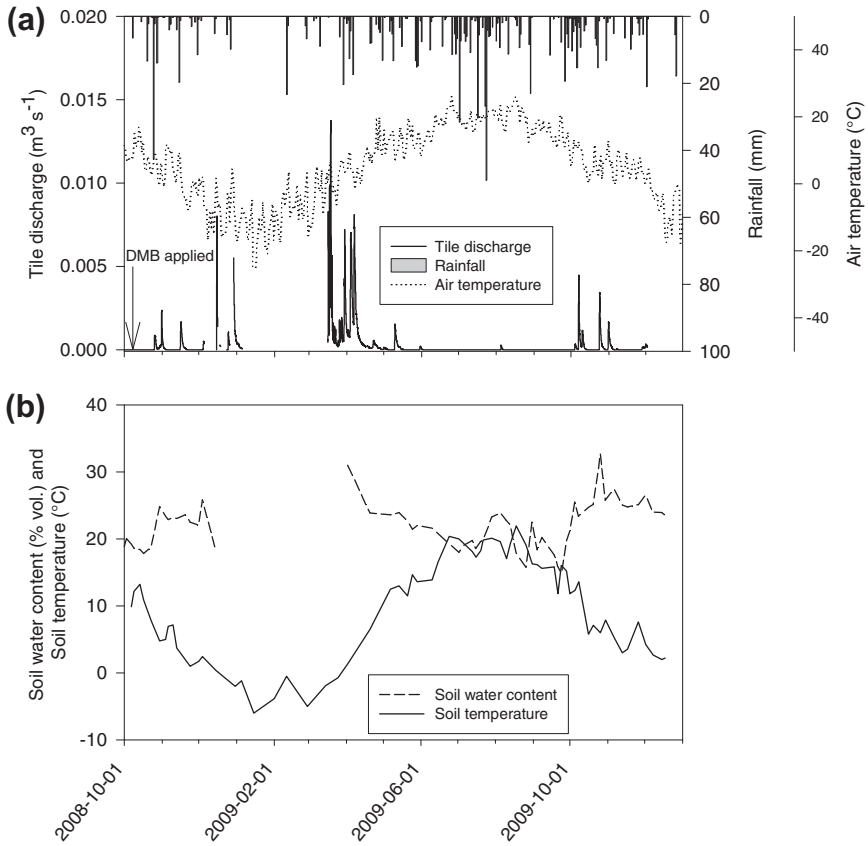

Fig. 2. (a) Tile discharge, rainfall and average daily air temperature for the 2008–2009 study period, and (b) soil temperature and soil water contents measured at 0.25 m depth in the soil for the 2008–2009 study period. Dates to be read as yyyy-mm-dd. Tile discharge monitoring was suspended over the winter months due to freezing temperatures.

concentration × collection interval (30 min)) are also given in Table 4a. No PPCPs were ever found above detection limits in tile drainage from the reference field section (i.e. section 4), where no DMB was applied.

None of the selected PPCPs (Table S1) were present above detection limits in groundwater samples prior to DMB application for either field section. Post-DMB application, only ibuprofen, triclosan, triclocarban, and O-desmethyl venlafaxine were detected once in groundwater; 2 d after the first rain event post-application (24 DPA) that induced tile flow (Table 4b) at 2 m depth at low ng L^{-1} levels. No PPCPs were found above detection limits in groundwater samples from the reference field section, or ever at the 4 m or 6 m piezometer depths in field section 1 where DMB was applied.

3.5. PPCPs in wheat grain

Wheat planted over field sections 1, 2, 3, and 4 was harvested in September 2009. None of the selected PPCPs (Table S1) were found in grain samples above detectable limits from either field section 1 where DMB was applied or the reference field section.

4. Discussion

The limited detection of the selected PPCPs in both groundwater and tile water could be related to a combination of sorption characteristics of the PPCPs, as well as interacting soil factors governing contaminant transport/sequestration, degradation/transformations of PPCPs, and the processes governing the physical breakdown of the DMB. Most of the PPCPs we focused on in our water analyses that were not detected in any tile water or groundwater samples (e.g. fluoxetine, miconazole, tetracyclines, fluoroquinolones), had relatively higher reported $\log K_{ow}$ values (i.e. >4), indicating a high sorption potential due to hydrophobic partitioning, and/or high $\log K_{oc}$ values (i.e. >4), indicating strong sorption onto organic matter (Tolls, 2001; Kinney et al., 2006a; Kwon and Armbrust, 2008; Kim et al., 2009). These PPCPs (fluoxetine, miconazole, tetracyclines, fluoroquinolones) may have been more strongly bound to DMB, which may account, at least partially, for their lack of detection in tile and groundwater samples as well as their long-term detection in incorporated DMB. The analgesic (acetaminophen and ibuprofen) and anticonvulsant compounds (carbamazepine) detected in water have relatively low reported $\log K_{ow}$ and $\log K_{oc}$ values (Scheytt et al., 2005; Yamamoto et al., 2009), while the bacteriocides (triclosan and triclocarban) have relatively high $\log K_{ow}$ and $\log K_{oc}$ values (Halden and Paull, 2005; Agyin-Birikorang et al., 2010). Both triclosan and triclocarban were present at much higher concentrations in the DMB than the other PPCPs detected in water samples, which may account for their detection in this study. Also, the pH of the DMB (7.9) is near the pK_a of triclosan of 8.1 (Tixier et al., 2002), so much of the triclosan could have been in its anionic form, making it more soluble than indicated by $\log K_{ow}$ and $\log K_{oc}$ values. Citalopram and venlafaxine were also detected in water, despite reported high $\log K_{oc}$ values for this class of compounds (Kwon and Armbrust, 2008), suggesting other factors were likely more responsible for their mobility.

The study by Edwards et al. (2009) examined PPCP residuals in tile drainage effluents for several months following a summer DMB application of ~8 Mg dw ha^{-1}. In that study, PPCPs were detected

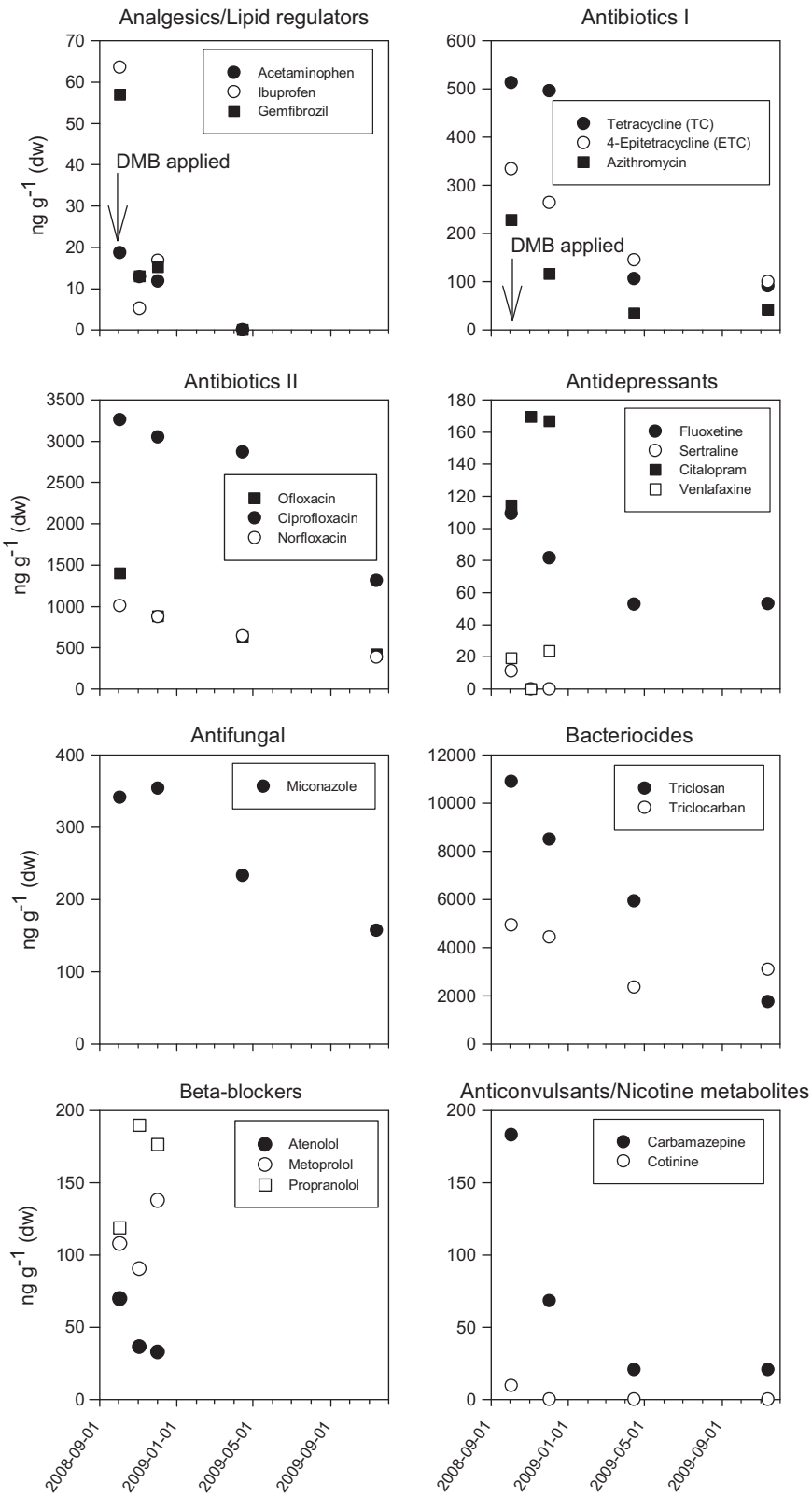

Fig. 3. Concentrations of PPCPs in DMB aggregates incorporated in the soil throughout the 2008–2009 study period. Dates to be read as yyyy-mm-dd.

in tile water after the first rain event at higher concentrations than those seen here, and several PPCPs (such as acetaminophen, carbamazepine and triclosan) were continuously detected in tile drainage after many months of monitoring. In the current study, DMB was applied in fall at ~3 times the rate used in the study by Edwards et al. (2009), yet PPCPs were detected on only one occasion in tile drainage (except for carbamazepine as noted above), and at comparatively lower concentrations. Although not entirely clear at this point, the difference in observed PPCPs in tile drainage between these two studies could, partially, be attributed to a com-

Table 3
Results of significant ($p \leqslant 0.05$) regression analysis conducted on PPCP concentrations in incorporated DMB aggregates over the study period to model dissipation; an exponential decay model ($y = ae^{-kt}$) was used (y = concentration in ng g^{-1}, t = days post-application, k = decay constant in d^{-1}).

Compound	Equation	Half-life (d) ln(2)/k	R^2	p
Analgesics				
Acetaminophen	$y = 19.1e^{-0.011t}$	63	0.95	0.03
Ibuprofen	$y = 63.5e^{-0.058t}$	12	0.90	0.05
Lipid regulators				
Gemfibrozil	$y = 56.2e^{-0.035t}$	20	0.94	0.03
Anticonvulsants				
Carbamazepine	$y = 181.7e^{-0.015t}$	46	0.97	0.02
Antifungals				
Miconazole	$y = 362.3e^{-0.002t}$	347	0.94	0.03
Antibiotics				
Norfloxacin	$y = 1011.1e^{-0.0024t}$	289	0.99	<0.0001
Ofloxacin	$y = 1282.1e^{-0.0035t}$	198	0.90	0.049
Azithromycin	$y = 223.9e^{-0.0097t}$	71	0.94	0.03
Epitetracycline	$y = 327.8e^{-0.0035t}$	198	0.97	0.01
Bacteriocides				
Triclosan	$y = 10931.4e^{-0.0038t}$	182	0.98	0.01

bination of: (i) modest differences in the depth of tile drains at each site (~0.8 m depth in Edwards et al. (2009) study), (ii) differences in the soil physical characteristics between the two study sites (e.g., lower degree of soil macroporosity and preferential flow, and augmented matrix flow induced by the lighter textured soils in this study), (iii) the tillage approaches used to incorporate the biosolids in the soil, (iv) the time of year the applications were conducted (fall to winter (current study) vs. summer to winter (Edwards et al., 2009)), and (v) differences in the consistency or rheological properties of the DMB.

Much of the transport of PPCPs to tile drains in the Edwards et al. (2009), Lapen et al. (2008), and Larsbo et al. (2009) studies occurred via preferential flow through vertical macropores (primarily earthworm burrows) that span an observed depth of over 1 m in the soil. Large macropores can promote transport of colloid and non-colloidal contaminants to depth in the soil profile (de Jonge et al., 2004; Jarvis, 2007). These macropores reduced bulk PPCP sorption in the soil profile above the tiles, as well as facilitated very rapid transport of PPCPs to tile drain depth and below (Larsbo et al., 2009). Moreover, surface soils in the Edwards et al. (2009) study site were more clayey, and macropores (earthworm burrows in particular) as a result, were found to maintain their integrity over long periods of time (unpublished data). Field soils in this study are, overall, lighter in texture (Table 1). This may have promoted matrix sorption and a higher degree of soil matrix flow relative to macropore flow, thereby reducing preferential flow via macropores to depth in the soil (Jarvis, 2007). All of these factors would have reduced PPCP transport to tile drain and shallow ground water depth. Further, the mouldboard plowing method used to incorporate the applied DMB in this study could have disrupted the macropores connected to the surface to a much more efficient degree than the incorporation methods employed by Edwards et al. (2009); which included directly injecting the DMB at about 0.11 m below the soil surface, and surface spreading followed by passes with a cultivator to mix the DMB into the shallow surface soils. Because the incorporation approach in Edwards et al. (2009) was shallower it allowed for many DMB aggregates to be exposed at the soil surface, therefore providing more exposure to direct weathering and leaching processes; this, coupled with the timing of the DMB application (summer), promoted a greater degree of biological activity to break down aggregates and release bound PPCPs, relative to the cooler fall-winter application in this study. Finally, different characteristics in the DMB itself could have had an impact on the decomposition of DMB and the release of PPCPs into the soil and soil water system. The ROPEC DMB had a much more cake-like consistency relative to the DMB sourced in the Edwards et al. (2009) study, which had a more gelatinous texture which was found to increase aggregate surface area (relative to ROPEC DMB) (unpublished data).

The observed PPCP losses in the incorporated DMB over time did not appear to be due mainly to mobilization/transport of these compounds, given their transient detection at low ng L^{-1} levels in both tile effluent and shallow groundwater, limited detection in soil cores, as well as their non-detection in grain samples. Dissipation of PPCPs, through degradation or transformation of the parent compounds, as the DMB degraded in the soil is a plausible cause of the reductions in these compounds over time. Naproxen has been shown to be rapidly mineralized in a variety of soil types, with the

Table 4
PPCPs detected in tile water (a) and groundwater (b) post-DMB application (ng L^{-1}).

(a) Tile water

Compound	Concentration	Time detected (days post-application)	Mass load (ng 30 min^{-1})
Anticonvulsants			
Carbamazepine	13, 5	22, 73	8700, 6515
Analgesics			
Acetaminophen	13	22	8500
Ibuprofen	24	22	16000
Bacteriocides			
Triclosan	73	22	48000
Triclocarban	40	22	26000
Antidepressants			
O-desmethyl Venlafaxine	74	22	48000
Venlafaxine	33	22	22000
Citalopram	24	22	16000

(b) Groundwater

Compound	Concentration	Time detected (days post-application)	Depth detected (m)
Analgesics			
Ibuprofen	10	24	2
Bacteriocides			
Triclosan	19	24	2
Triclocarban	12	24	2
Antidepressants			
O-desmethyl Venlafaxine	13	24	2

Note: Please see Table S1 for a complete list of PPCPs analyzed in water samples.

highest rates of mineralization achieved when incubated at 30 °C and approximately 15% soil moisture, corresponding to a half-life of ~2 d (Topp et al., 2008a). Our previous study showed that the addition of liquid biosolids to the soil increased the rate of mineralization, especially at lower incubation temperatures (Topp et al., 2008a), indicating that the microbial population in the biosolids contributes to naproxen degradation. Soil water contents at the study site were somewhat higher than the optimal level indicated for the loam soil studied in Topp et al. (2008a), ranging between 16% and 28% in the weeks following DMB application at 0.25 m depth (DMB was incorporated to 0.2 m). Observed soil temperatures at this depth were also much lower than optimal, ranging between 0 and 13 °C. However the additional microbes present in the DMB may have contributed to more rapid degradation of PPCPs that are susceptible to microbial degradation. The lighter textured soil at this site, relative to the Edwards et al. (2009) site, may have also facilitated microbial degradation. In this case, it appears that cotinine, acetaminophen, gemfibrozil and ibuprofen may have been more rapidly dissipated, as indicated by their non-detection in incorporated DMB samples within 6 months post-application. Some of the more persistent compounds in the DMB, however, such as triclocarban and triclosan, have reported half-lives, in aerated soil, of 108 and 18 d, respectively (Ying et al., 2007). These antimicrobial compounds have also been found to be more persistent when applied to soils as part of DMB (vs. LMB or direct incorporation into soil), which is related to high sorption onto DMB organic matter and resulting reduced bioavailability (Al-Rajab et al., 2009). There have been similar findings for fluoroquinolones, where persistence of these antibiotics was observed in soil post-land application of biosolids at 5 and 21 months post-application, with limited mobility into subsoil due to high sorption onto organic matter in the biosolids (Golet et al., 2003). Those PPCPs with greater sorption to DMB (tetracyclines, fluoroquinolones, miconazole, fluoxetine, triclosan and triclocarban) may therefore have been slower to degrade as a result of reduced bioavailability to soil microorganisms, and this appears to be consistent with observed PPCP concentrations in incorporated DMB over time. The formation of non-extractable residues may also explain reductions in PPCP concentrations in incorporated DMB and limited detection in soil core samples over the course of the study. Studies on the fate of clotrimazole (Sabourin et al., 2011), and triclosan and triclocarban (Al-Rajab et al., 2009) point to these non-extractable residues as a potential sink for PPCPs in soil.

The estimated dissipation rates in this study were lower than those reported in some controlled laboratory experiments (e.g. Topp et al., 2008a; Xu et al., 2009; Kwon et al., 2010). However, the rates reported in this study were higher than those from a long-term study of PPCP loss in outdoor soil mesocosms (Walters et al., 2010). Some of the same general trends were observed, however, with miconazole and fluoroquinolones having the lowest dissipation rates in this study and Walters et al. (2010). We expected dissipation of PPCPs in this study to be limited, in part, by: cooler soil temperatures, minimal rainfall in winter reducing transport, and the mode of soil incorporation.

Nevertheless, the incorporated DMB aggregates could serve as a reservoir of PPCPs for water contamination nearly a year after application. For two of the most persistent drugs found in this study, fluoxetine and miconazole, loading rates on the day of application were estimated (assuming a measured dry bulk density of the DMB of ~0.3 g cm^{-3} and estimates of an effective 'uniform' depth of DMB at plow depth) at 2.4×10^{-3} kg ha^{-1} and 8×10^{-3} kg ha^{-1}, respectively; based on an application rate of 22 Mg dw ha^{-1}. We estimated the remaining amount of fluoxetine and miconazole in the aggregates at each monitoring time period. At ~2 months post-application (assuming a uniform DMB depth of 0.7 cm at incorporation depth and bulk density values above), amounts were ~1.8×10^{-3} and 7.8×10^{-3} kg ha^{-1}, for fluoxetine and miconazole, respectively, and at ~1 year post-application (assuming a uniform DMB depth of 0.3 cm at incorporation depth and bulk density values above), 4.8×10^{-4} and 1.4×10^{-3} kg ha^{-1}, respectively. Although detectable amounts of PPCPs remained in DMB aggregates incorporated in the soil over a 1 year period, these reservoirs did not appear to be a risk to water receptors.

Although uptake of PPCPs by various plant species has been documented (Boxall et al., 2006; Wu et al., 2010), soils or nutrient solutions used for these laboratory studies were typically spiked with PPCPs to levels much higher than would be found in biosolids, which may account for the observed uptake. Under the field conditions of our study, however, even applying the maximum allowable amount of biosolids, no PPCP uptake was observed in wheat grain (grown in the spring following DMB application the previous fall). This is likely related to the low PPCP mobility, and degradation/formation of non-extractable residues that also limited observed PPCP concentrations in water, as well as the additional dilution of PPCPs as the DMB was mixed with surrounding soils. This factor would have further limited direct root zone contact with incorporated DMB.

5. Conclusions

Despite the relatively high rates of DMB applied at the site (22 Mg dw ha^{-1}), there was no significant impact on the quality of either tile drainage or groundwater. PPCPs were detected in incorporated DMB aggregates up to 1 year post-application, but reductions in concentrations over the course of the study did not appear to be due to mobilization into either tile or groundwater, as confirmed by their limited detection in these water receptors, both in frequency and concentration. Additionally, there were no observed PPCPs in the grain of wheat planted the spring following application. This application, did not pose a significant risk to surface or groundwater resources at this site. Several of the mechanisms that were deemed to limit tile and groundwater contamination in this study, relative to the Edwards et al. (2009) study, were: (i) slightly deeper tile drainage systems, (ii) fewer macropores facilitating preferential flow, (iii) lighter textured soils promoting soil matrix sorption and compound sequestration, (iv) the tillage approaches used to incorporate DMB reducing preferential flow and exposure to weathering/leaching elements at the soil surface, (v) the cooler temperatures reducing decomposition of the DMB and release of parent compounds, (vi) differences in the consistency or rheological properties of the DMB, and (vii) limited rainfall precipitation in winter reducing physical breakdown and transport of PPCPs.

Acknowledgements

This work was financially supported by Agriculture and Agri-Food Canada's SAGES initiative, and the Ontario Ministry of the Environment. We also appreciate the support and advice provided by the City of Ottawa.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.12.018.

References

Agyin-Birikorang, S., Miller, M., O'Connor, G.A., 2010. Retention-release characteristics of triclocarban and triclosan in biosolids, soils, and biosolids-amended soils. Environ. Toxicol. Chem. 29, 1925–1933.

Al-Rajab, A.J., Sabourin, L., Scott, A., Lapen, D.R., Topp, E., 2009. Impact of biosolids on the persistence and dissipation pathways of triclosan and triclocarban in an agricultural soil. Sci. Total Environ. 407, 5978–5985.
Boxall, A.B.A., Johnson, P., Smith, E.J., Sinclair, C.J., Stutt, E., Levy, L.S., 2006. Uptake of veterinary medicines from soils into plants. J. Agric. Food. Chem. 54, 2288–2297.
de Jonge, L.W., Kjaergaard, C., Moldrup, P., 2004. Colloids and colloid-facilitated transport of contaminants in soils: an introduction. Vadose Zone J. 3, 321–325.
Edwards, M., Topp, E., Metcalfe, C.D., Li, H., Gottschall, N., Bolton, P., Curnoe, W., Payne, M., Beck, A., Kleywegt, S., Lapen, D.R., 2009. Pharmaceutical and personal care products in tile drainage following surface spreading and injection of dewatered municipal biosolids to an agricultural field. Sci. Total Environ. 407, 4220–4230.
Ellis, J.B., 2006. Pharmaceutical and personal care products (PPCPs) in urban receiving waters. Environ. Pollut. 144, 184–189.
Environment Canada, 2011. Canadian Climate Normals 1971–2000. <climate.weatheroffice.gc.ca/climate_normals>.
Golet, E.M., Xifra, I., Siegrist, H., Alder, A.C., Giger, W., 2003. Environmental exposure assessment of fluoroquinolone antibacterial agents from sewage to soil. Environ. Sci. Technol. 37, 3243–3249.
Halden, R.U., Paull, D.H., 2005. Co-occurrence of triclocarban and triclosan in US water resources. Environ. Sci. Technol. 39, 1420–1426.
Halling-Sorensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Lutzhoft, H.C.H., Jorgensen, S.E., 1998. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. Chemosphere 36, 357–393.
Jarvis, N.J., 2007. A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. Eur. J. Soil Sci. 58, 523–546.
Jjemba, P.K., 2006. Excretion and ecotoxicity of pharmaceutical and personal care products in the environment. Ecotoxicol. Environ. Saf. 63, 113–130.
Kim, H.J., Lee, H.J., Lee, D.S., Kwon, J.H., 2009. Modeling the fate of priority pharmaceuticals in Korea in a conventional sewage treatment plant. Environ. Eng. Res. 14, 186–194.
Kinney, C.A., Furlong, E.T., Werner, S.L., Cahill, J.D., 2006a. Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. Environ. Toxicol. Chem. 25, 317–326.
Kinney, C.A., Furlong, E.T., Zaugg, S.D., Burkhart, M.R., Werner, S.L., Cahill, J.D., Jorgensen, G.R., 2006b. Survey of organic wastewater contaminants in biosolids destined for land application. Environ. Sci. Technol. 40, 7207–7215.
Kwon, J.W., Armbrust, K.L., 2008. Aqueous solubility, *n*-octanol–water partition coefficient, and sorption of five selective serotonin reuptake inhibitors to sediments and soils. Bull. Environ. Contam. Toxicol. 81, 128–135.
Kwon, J.W., Armbrust, K.L., Xia, K., 2010. Transformation of triclosan and triclocarban in soils and biosolids-applied soils. J. Environ. Qual. 39, 1139–1144.
Langdon, K.A., Warne, M.S., Kookana, R.S., 2010. Aquatic hazard assessment for pharmaceuticals, personal care products, and endocrine-disrupting compounds from biosolids-amended land. Integr. Environ. Assess. Manage. 6, 663–676.
Lapen, D.R., Topp, E., Metcalfe, C.D., Li, H., Edwards, M., Gottschall, N., Bolton, P., Curnoe, W., Payne, M., Beck, A., 2008. Pharmaceutical and personal care products in tile drainage following land application of liquid municipal biosolids. Sci. Total Environ. 399, 50–65.
Larsbo, M.L., Lapen, D.R., Topp, E., Metcalfe, C.D., Abbaspour, K.C., Fenner, K., 2009. Simulation of pharmaceutical and personal care product transport to tile drains after biosolids application. J. Environ. Qual. 38, 1274–1285.
Lishman, L., Smyth, S.A., Sarafin, K., Kleywegt, S., Toito, J., Peart, T., Lee, B., Servos, M., Beland, M., Seto, P., 2006. Occurrence and reductions of pharmaceuticals and personal care products and estrogen by municipal wastewater treatment plants in Ontario, Canada. Sci. Total Environ. 367, 544–558.
Lozano, N., Rice, C.P., Ramirez, M., Torrents, A., 2010. Fate of triclosan in agricultural soils after biosolid applications. Chemosphere 78, 760–766.
Metcalfe, C.D., Alder, A.C., Halling-Sorensen, B., Krogh, K., Fenner, K., Larsbo, M., et al., 2009. Exposure assessment methods for veterinary and human-use medicines in the environment: PEC vs. MEC comparisons. In: Kummerer, K. (Ed.), Pharmaceuticals in the Environment: Sources, Fate, Effects and Risks, third ed. Springer, Berlin, Heidelberg, pp. 147–171.
Metcalfe, C.D., Chu, S., Judt, C., Li, H., Oakes, K.D., Servos, M.R., Andrews, D.M., 2010. Antidepressants and their metabolites in municipal wastewater, and downstream exposure in an urban watershed. Environ. Toxicol. Chem. 29, 79–89.
Musolff, A., Leschik, S., Moder, M., Strauch, G., Reinstorf, F., Schirmer, M., 2009. Temporal and spatial patterns of micropollutants in urban receiving waters. Environ. Pollut. 157, 3069–3077.
Ministry of the Environment. Ontario Regulation 267/03. January 2011.
O'Connor, G.A., Elliott, H.A., Basta, N.T., Bastian, R.K., Pierzynski, G.M., Sims, R.C., Smith Jr., J.E., 2005. Sustainable land application: an overview. J. Environ. Qual. 34, 7–17.
Onesios, K.M., Yu, J.T., Bouwer, E.J., 2009. Biodegradation and removal of pharmaceuticals and personal care products in treatment systems: a review. Biodegradation 20, 441–466.
Sabourin, L., Beck, A., Duenk, P.W., Kleywegt, S., Lapen, D.R., Li, H., Metcalfe, C.D., Payne, M., Topp, E., 2009. Runoff of pharmaceuticals and personal care products following application of dewatered municipal biosolids to an agricultural field. Sci. Total Environ. 407, 4596–4604.
Sabourin, L., Al-Rajab, A.J., Chapman, R., Lapen, D.R., Topp, E., 2011. Fate of the antifungal drug clotrimazole in agricultural soil. Environ. Toxicol. Chem. 30, 582–587.
Scheurer, M., Ramil, M., Metcalfe, C.D., Groh, S., Ternes, T.A., 2010. The challenge of analyzing beta-blocker drugs in sludge and wastewater. Anal. Bioanal. Chem. 396, 845–856.
Scheytt, T., Mersmann, P., Lindstadt, R., Heberer, T., 2005. 1-Octanol/water partition coefficients of 5 pharmaceuticals from human medical care: carbamazepine, clofibric acid, diclofenac, ibuprofen, and propyphenazone. Water Air Soil Pollut. 165, 3–11.
Spongberg, A.L., Witter, J.D., 2008. Pharmaceutical compounds in the wastewater process stream in Northwest Ohio. Sci. Total Environ. 397, 148–157.
Tixier, C., Singer, H.P., Canonica, S., Müller, S.R., 2002. Phototransformation of triclosan in surface waters: a relevant elimination process for this widely used biocide-laboratory studies, field measurements, and modeling. Environ. Sci. Technol. 36, 3482–3489.
Tolls, J., 2001. Sorption of veterinary pharmaceuticals in soils: a review. Environ. Sci. Technol. 35, 3397–3406.
Topp, E., Hendel, J.G., Lapen, D.R., Chapman, R., 2008a. Fate of the nonsteroidal anti-inflammatory drug naproxen in agricultural soil receiving liquid municipal biosolids. Environ. Toxicol. Chem. 27, 2005–2010.
Topp, E., Monteiro, S.C., Beck, A., Coelho, B.B., Boxall, A.B.A., Duenk, P.W., Kleywegt, S., Lapen, D.R., Payne, M., Sabourin, L., Li, H., Metcalfe, C.D., 2008b. Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field. Sci. Total Environ. 396, 52–59.
USEPA, 2007. Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS. EPA-821-R-08-002.
Walters, E., McClellan, K., Halden, R.U., 2010. Occurrence and loss over three years of 72 pharmaceuticals and personal care products from bioslids–soil mixtures in outdoor mesocosms. Water Res. 44, 6011–6020.
Wu, C., Spongberg, A.L., Witter, J.D., Fang, M., Czajkowski, K.P., 2010. Uptake of pharmaceutical and personal care products by soybean plants from soils applied with biosolids and irrigated with contaminated water. Environ. Sci. Technol. 44, 6157–6161.
Xia, K., Bhandari, A., Das, K., Pillar, G., 2005. Occurrence and fate of pharmaceutical and personal care products (PPCPs) in biosolids. J. Environ. Qual. 34, 91–104.
Xu, J., Wu, L., Chang, A.C., 2009. Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils. Chemosphere 77, 1299–1305.
Yamamoto, H., Nakamura, Y., Moriguchi, S., Nakamura, Y., Honda, Y., Tamura, I., Hirata, Y., Hayashi, A., Sekizawa, J., 2009. Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: laboratory photolysis, biodegradation, and sorption experiments. Water Res. 43, 351–362.
Ying, G.G., Yu, X.Y., Kookana, R.S., 2007. Biological degradation of triclocarban and triclosan in a soil under aerobic and anaerobic conditions and comparison with environmental fate modelling. Environ. Pollut. 150, 300–305.