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TECHNICAL REPORT

Organic Compounds in the Environment

Using the Pesticide Toxicity Index to show the potential ecosystem benefits of on-farm biobeds

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Abstract

The influent and effluent of two single-cell biobeds (Province of Alberta, Canada) and two dual cell-biobeds (Province of Saskatchewan, Canada) were monitored during a number of growing seasons. A total of 59 unique pesticide active ingredients were detected, with all biobed influent samples ($n = 54$) and 93% of effluent samples ($n = 54$) containing pesticide mixtures. About one-half of the effluent samples in both single-cell (56%) and dual-cell (45%) biobeds contained active ingredients that have Groundwater Ubiquity Score (GUS) values >2.8 and so were more likely to move through the biomatrix materials into effluent. The Pesticide Toxicity Index (PTI) calculated for aquatic indicator species (i.e., vascular and nonvascular plants, invertebrates, and fish) was always larger for influent samples (e.g., median PTI >500 for invertebrates in dual-cell biobed) than effluent samples (i.e., median PTI <1). As such, this study demonstrates the potential ecosystem benefits of the broad adoption of on-farm biobeds in the Canadian Prairies for recycling tank rinsate as a strategy to accelerate a green economy. Although biobeds were highly effective in reducing the concentrations for pesticides with a wide range of soil organic carbon coefficient and half-life values, the biobed effectiveness was relatively poor for the herbicides clopyralid, diclofop, fluroxypyr, and imazethapyr. Clopyralid (3.02), fluroxypyr (3.70), and imazethapyr (3.90) all have relatively high GUS values (>2.8) and are thus more likely to be detected in effluent than active ingredients with smaller GUS values. This suggests that further improvements in biosystem design need to be made for optimizing the recycling of these pesticides.

1 | INTRODUCTION

Pesticide handling areas result in point-source pollution that can account for up to 90% of the total pesticide loadings in water resources (Frede et al., 1998; Neumann et al., 2002). By capturing the pesticide residues associated with the filling and cleaning of spraying equipment, biobeds are designed to minimize this point-source pollution (Torstensson, 2000). A biobed is an above-ground or in-ground container structure that holds a biomixture that is typically derived from a combination of plant dry matter (e.g., straw), humified organic matter (e.g., peat), and soil. Previous studies have shown that the retention and degradation of pesticides in a biomatrix are influenced by the physico-chemical properties of the pesticide (e.g., half-life, sorption coefficient), the composition of the biomatrix (i.e., only soil vs. mixture of plant dry matter and humified substrate), biobed water management

Abbreviations: 2,4-D, 2,4-dichlorophenoxyacetic acid; DT_{50}, soil pesticide half-life; GUS, Groundwater Ubiquity Score; MCPA, 2-methyl-4-chlorophenoxyacetic acid; PTI, Pesticide Toxicity Index.

(i.e., frequency and volume of wastewater loading), and other factors (e.g., ambient temperature) (Cooper et al., 2016; Coppola et al., 2007; Delgado-Moreno et al., 2017; Karanasios et al., 2012; Knight et al., 2016; Lescano et al., 2018; Spliid et al., 2006).

Invented by a Swedish farmer in the 1990s, on-farm biobeds have been adopted in Europe (Karanasios et al., 2012) but remain largely unknown to farmers in Canada, who operate a combined 37.8 million ha of cropland (Braul et al., 2018). About 83% of Canada's cropland is located in the Prairies, and four on-farm biobeds became operational in 2014 and 2015 (Table 1). The construction, maintenance, and operation of the four biobeds followed guidelines developed for the Canadian Prairies (Braul et al., 2018). This study evaluates the effectiveness of these biobeds to process rinsate containing pesticides typically applied in Prairie agricultural and nonagricultural applications. Pesticides most frequently applied to the biobeds included herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D), bromoxynil, clopyralid, 2-methyl-4-chlorophenoxyacetic acid (MCPA), and mecoprop.

A parameter for predicting the relative ranking of pesticides moving toward groundwater is the Groundwater Ubiquity Score (GUS) or Tier-1 assessments (Hall et al., 2015; Kolupaeva et al., 2019). The GUS score is calculated by $[\log(DT_{50}]\times[4 - \log(K_{oc})]$, where DT_{50} is the soil half-life of the pesticide and K_{oc} is the normalized organic carbon sorption coefficient (Gustafson, 1989). Groundwater Ubiquity Score values >2.8 indicate that a pesticide has a high potential to move to groundwater (Close & Humphries, 2019; Laabs et al., 2002; Soares et al., 2012; Zambito Marsala et al., 2020; Zheng & Cooper, 1996). Given that GUSs provide for relative measures of pesticide movement through a matrix such as soil, we hypothesize that the pesticides detected in biobed effluents are more likely to be pesticides that have greater GUS values.

The Pesticide Toxicity Index (PTI) is a known tool to quantify the relative toxicity of pesticide mixtures to indicator species of aquatic organisms. The PTI is a Tier-1–type assessment that combines measured pesticide concentrations with acute toxicity database values through an additive toxic-unit model (Munn et al., 2010; Nowell et al., 2014). In a river water study, a variety of pesticide mixtures were detected depending on sampling location and time, and the PTI was used to compare the relative risk of these pesticide mixtures to aquatic organisms (Nowell et al., 2014). For Prairie rivers, PTI values tend to be larger for nonvascular and vascular plants than for invertebrates or fish because pesticide mixtures in Prairie rivers tend to be dominated by herbicides (e.g.,2,4-D, bentazone, clopyralid, fluroxypyr, and MCPA) rather than insecticides or fungicides (Challis et al., 2018; Gamhewage et al., 2021; Rawn et al., 1999). In this study, we quantified the PTIs for samples containing pesticide mixtures and hypothesized that in all cases (nonvascular plants, vascular plants, invertebrates, and fish) the mean PTI of biobed effluent will be significantly smaller than the mean PTI of biobed influent.

Core Ideas

- Both single-cell and dual-cell biobeds performed remarkably in colder climates (Canadian Prairies).
- Pesticides detected in effluents were more likely to be pesticides that have greater GUS values.
- The Pesticide Toxicity Index (PTI) was drastically smaller for biobed effluent than for influent.
- The broad adoption of biobeds for recycling tank rinsate will contribute to a green economy.
- The biobed system design must be refined to broaden its effectiveness to treat all pesticides.

The objective of this study was to measure, through quantifying pesticide concentrations and PTI values, the efficiency of single-cell and dual-cell biobeds as it applies to pesticides commonly used in Prairie agriculture.

2 | MATERIALS AND METHODS

2.1 | Sampling and pesticide analysis

This study included two single-cell biobeds located in the Province of Alberta and two dual-cell biobeds in the Province of Saskatchewan (Table 1). Although there were differences in biobed configurations, particularly between provinces, biomixtures always had a 2:1:1 ratio by volume of plant dry matter (i.e., straw or wood), humified organic matter (i.e., peat or compost), and local topsoil. At each site, pesticide rinsate was collected and held in storage influent tanks and then drip-irrigated or manually applied onto the surface of the biomatrix in the single-cell biobeds in Alberta or onto the first cell of the dual-cell biobeds in Saskatchewan. The outflow of the first cell was further drip-irrigated onto the surface of the second biobed cell. The outflow of single-cell biobeds in Alberta or the second cell of dual cell biobeds in Saskatchewan was directed to storage effluent tanks and held to facilitate sampling. For each of 54 sampling times in total, samples from influent and effluent storage tanks were collected in 1-L amber glass bottles on the same day and kept at 4 °C to quantify pesticide residues within 3 d from the time of collection. Pesticides detected in influent were considered an indication of the types and concentrations of the pesticides added to a biobed. Pesticides detected in effluent were

TABLE 1 Summary information of the four biobeds included in this study

Location	Biomatrix (2:1:1)	Surface area	Sampling period (no. of samples)
		m^2	
Single-cell biobeds in the Province of Alberta			
Grand Prairie[a]	wheat straw, compost, soil	44	Aug. 2015–Oct. 2015 (8)
			Aug. 2016–Oct. 2016 (8)
Vegreville[b]	wheat straw, peat, soil	8	June 2015–Aug. 2015 (12)
			June 2016–Sept. 2016 (16)
			July 2017–Aug. 2017 (8)
Dual-cell biobeds in the Province of Saskatchewan			
Outlook[b]	wood chips, peat, soil	6	July 2014–Sept. 2014 (8)
			June 2015–Sept. 2015 (14)
			June 2016–Sept. 2016 (14)
Simpson[b]	wood chips, peat, soil	4.5	July 2015–Sept. 2015 (8)
			June 2016–Sept. 2016 (12)

[a]Belowground biobed. [b]Aboveground biobed.

considered an indication of the types and concentrations of the pesticides not degraded or retained by the biobed.

All mass spectrometric analyses were conducted by the ISO17025 federal government laboratory Lethbridge Research and Development Centre in Agriculture and Agri-food Canada using validated in-house quantitative methods, including multiple reaction monitoring and surrogate internal standards. Samples were extracted and analyzed for 142–160 compounds (i.e., an increasing number of compounds in more recent years),and this multi-residue method has been previously published (Bergsveinson et al., 2018; Gamhewage et al., 2019; Munira et al., 2018). Briefly, samples were filtered (glass wool), acidified to pH 2 (sulfuric acid), and extracted from water using liquid–liquid partitioning with dichloromethane. Extracts were dried (acidified Na_2SO_4),concentrated, methylated (diazomethane), neutralized (hexane), and adjusted to 10 ml using rotary evaporator. Esterified extracts were injected (2 µl) in an Agilent 7890B gas chromatograph coupled with a 7000C QQQ mass selective detector and multiple reaction monitoring and an HP-5MS UI (30 m by 0.25 mm by0.25 µm) column.The temperature programming was 70 ˚C for 2 min, ramp of 25 ˚C min^{-1} to 150 ˚C, ramp of 3 ˚C min^{-1} to 200 ˚C, and ramp of 8 ˚C min^{-1} to 280 ˚C for 7 min, for a total run time of 38.86 min. Compounds were identified at the expected retention time by monitoring one target ion and at least two qualifier ions. The lower limit of quantification was 25 ngL^{-1} for most pesticides, and detections below this limit were considered not detected. Glyphosate, which was detected in both biobed influent and effluent, was only included in the analytical suite in 2017; hence, data were relatively limited for this widely used herbicide in North America.

2.2 | Pesticide detections and calculated parameters

For each pesticide active ingredient detected in influent or effluent samples, values for its GUS, DT_{50}, and K_{oc} were obtained from the Pesticides Properties DataBase(Lewis et al., 2016). Values for K_{oc} values were not available in Pesticides Properties DataBasefor 15 pesticide active ingredients and in these cases, the pesticide K_{oc} value was calculated from the listed GUS and DT_{50} values. Pesticides detected in influent or effluent samples were assigned to one of four GUS categories (extremely low, <0; low, 0–1.8; moderate, 1.8–2.8; or high, >2.8)(NPIC, 2021). We here define GUS as relative likelihood of pesticides being detected in the biobed effluent. For example, a high GUS value would mean that there is a high potential of the pesticide to be detected in effluent because it is both persistent and mobile in the biobed. Categories of DT_{50} (low, <16 d; moderate, 16–59 d; high, >60 d) (NPIC, 2021) and K_{oc} (highly mobile,<10; mobile, 10–100; moderately mobile, 100–1,000; slightly mobile, 1,000–10,000; hardly mobile, 10,000–100,000; immobile, >100,000) (FAO, 2000) were also assigned based on literature-recommended classes.

For the two single-cell biobeds combined and the two dual cell biobeds combined, the relative proportions of the assigned categories were calculated for the influent and effluent separately. For example, for the influent of single-cell biobeds, the relative proportion of highly mobile pesticides (K_{oc} <10) was calculated by the sum of the number of highly mobile pesticides (K_{oc} <10) detected in influent samples divided by total detects in the influent and expressed as a percentage.

For PTI calculation, for each pesticide active ingredient detected in influent or effluent samples, the aquatic life benchmarks data were obtained from USEPA (2018). These benchmarks data are based on the toxicity values of selected indicator species in standardized tests, namely the acute 48–96h LC_{50} (lethal concentrations inducing 50% mortality) for fish (rainbow trout, fathead minnow, or bluegill) or aquatic invertebrates (midge, scud, or daphnids) or the acute <10d EC_{50} (effective concentration inducing 50% growth inhibition) for aquatic vascular (green algae or diatoms) or nonvascular (duckweed) plants. Toxicity quotients were calculated by dividing each pesticide concentration present in the influent or effluent by the aquatic life benchmarks data of indicator species relevant for that pesticide. The PTI was then calculated by summing the toxicity quotients of all pesticides in an influent or effluent sample. The 7% of effluent samples that did not contain pesticide mixtures were excluded from the PTI calculations.

2.3 | Statistical analysis

For each of the top five most frequently detected pesticide active ingredients in biobed influent, the PROC TTEST in SAS 9.4 for Windows (SAS Institute, 2013) with a significance threshold of $P < .05$ was used to determine significant differences in pesticide concentrations between biobed influent versus effluent. These analyses were done for all biobeds combined as well as for single-cell and dual-cell biobeds separately. Data from single-cell and dual-cell biobeds were kept separate for all other statistical analyses in which the PROC TTEST ($P < .05$) was used to determine significant differences between influent versus effluent samples for PTI values.

3 | RESULTS AND DISCUSSION

A large portion (87%) of the 58 (Supplemental Table S1) unique active ingredients detected in influent samples had concentrations >1 μg L^{-1}. Active ingredients were always detected as mixtures, with the number of unique active ingredients per influent sample ranging from 6 to 31. In total, 31 herbicides, 14 fungicides, 12 insecticides, as well as nematicide dichlofenthion were detected in influent. Only 40 unique active ingredients were detected in effluent, and almost one-third (64%) of these were detected at concentrations <1 μg L^{-1}. The majority (93%) of the effluent samples still contained pesticide mixtures ranging from 3 to 21 unique active ingredients per sample. However, three samples had zero detections, and another effluent sample had a single detection of 2,4-D at 0.02 μg L^{-1}. In total, 22 herbicides, 10 fungicides, 7 insecticides, as well as nematicide dichlofenthion were detected in effluent.

Of the top five most frequently detected active ingredients in biobed influent, the mean effluent concentrations of 2,4-D (2.6 μg L^{-1}), dicamba (16.4 μg L^{-1}), MCPA (124 μg L^{-1}), mecoprop (0.4 μg L^{-1}), and bromoxynil (0.8 μgL^{-1}) were significantly smaller than the mean influent concentrations of these active ingredients (2,4-D, 7,441 μg L^{-1};dicamba, 152.8 μg L^{-1};MCPA, 7,946 μg L^{-1};mecoprop, 134 μg L^{-1};and bromoxynil, 1,476 μg L^{-1}).When single-cell and dual-cell biobeds were considered separately, these differences remained significant for both types of biobeds except that the mean concentration of mecoprop was statistically similar in influent and effluent in the case of dual-cell biobeds. Although the total mean active ingredient concentration in influent was much larger for single-cell (4,390 μg L^{-1}) than for dual-cell (527 μg L^{-1}) biobeds (Figure 1), both single-cell and dual-cell biobeds appeared to be effective for a range of the same pesticides (Table 2). The mean active ingredient concentration in effluent was 286 μg L^{-1} for single-cell and 99 μg L^{-1} for dual-cell biobeds (Figure 1). Given that the single-cell biobeds had received pesticide concentrations in much greater concentrations than thedual-cell biobeds, we highlight that these data demonstrate that the single-cell biobeds performed remarkably well under Prairie conditions. This is the first study worldwide that allows for a comparison of the performances of single-cell versus dual-cell biobeds.

A total of 27 unique active ingredients were detected in single-cell influent, with detections being largest for the herbicides glyphosate (maximum, 76,798 μg L^{-1}), 2,4-D (69,561 μg L^{-1}), MCPA (67,030 μg L^{-1}), and clopyralid (37,971 μg L^{-1}) (Figure 1). Dual-cell influent received a much broader range of unique active ingredients ($n = 52$) but with a maximum detection of 30,543 μg L^{-1} (bentazone). Although 80% of the unique active ingredients detected in single-cell influent were also detected in single-cell effluent, dual-cell effluent only contained 65% of the unique active ingredients detected in dual-cell influent. The active ingredients that were detected in influent but not in effluent had a wide range of K_{oc}, DT_{50}, and GUS values. Effluents with no pesicide detected had GUS values <2.8; thus, none had a high potential of being detected in the biobed effluent (Table 3).

Biobeds were not fully efficient in recycling pesticide rinsate. Thirty-eight percent of the unique active ingredients detected in single-cell effluent had concentrations >1 μg L^{-1}, or nine active ingredients in total. This included MCPA in 55% of effluent samples as well as dicamba (42%), 2,4-D (14%), and mecoprop (10%). Thirty-three percent of the unique active ingredients detected in dual-cell effluent had concentrations >1 μg L^{-1} or 12 active ingredients in total, including MCPA (40%), 2,4-D (20%), dicamba (14%), and bromoxynil (9%). These active ingredients have typically short half-lives in soil (i.e., 1 d to 3.5 wk) (Lewis et al., 2016). For laboratory incubations, Ngombe et al. (2011) reported that almost all 2,4-D was degraded within 10 d after its incorporation into biomatrices. However, these auxin herbicides have

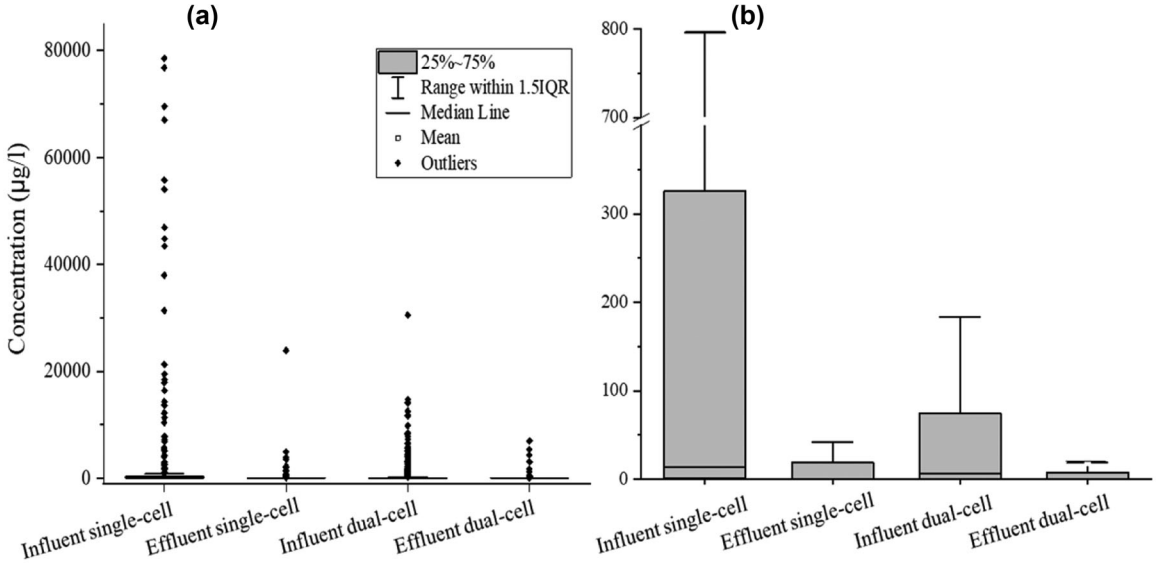

FIGURE 1 Concentrations of active ingredients in single-cell and dual-cell biobed influents and effluents with graphs showing (a) all outliers and (b) a closer view of the interquartile ranges (IQR)

TABLE 2 Mean concentration of 10 active ingredients in the influent of single-cell and dual-cell biobeds and the percent reduction of that mean concentration in the effluent

	Single-cell biobeds		Dual-cell biobeds	
Active ingredient	**Mean influent concentration**	**Reduction**	**Mean influent concentration**	**Reduction**
	µg L^{-1}	%	µg L^{-1}	%
Metolachlor	<1 (2)	100	142 (16)	99.23
Boscalid	208 (11)	100	30 (15)	99.91
Fenoxaprop	1,841 (13)	99.80	<1 (14)	100
EPTC	<1 (2)	100	1,845 (14)	99.95
Propiconazole	16 (13)	98.53	4 (17)	99.22
Bromoxynil	14 (15)	99.41	2,451 (21)	99.96
MCPA	13,206 (17)	98.28	2,734 (23)	99.45
2,4-D	14,695 (17)	100	2,105 (23)	99.79
Dichlofenthion	2 (8)	96.70	7 (18)	95.29
Dicamba	115 (8)	97.66	164 (26)	84.56

Note. A reduction of 100% indicates that the active ingredient is not detected in the effluent. Numbers in parentheses refer to the number of detections of the active ingredient in influent. 2,4-D, 2,4-dichlorophenoxyacetic acid; EPTC, S-ethyl dipropylthiocarbamate; MCPA, 2-methyl-4-chlorophenoxyacetic acid.

relatively large water solubility (i.e., >20,000 mgL^{-1}) (Lewis et al., 2016), which would make these active ingredients relatively mobile in the biobed, and hence they would appear in effluent rather than being fully degraded in the biobed.

The herbicide clopyralid was among the most frequently detected active ingredients in effluent (single-cell, 88% of effluent samples; dual-cell, 75%), while also being detected in among the largest concentrations (maximum concentrations: single-cell,23,898 µg L^{-1}; dual-cell, 3,044 µg L^{-1}). In dual-cell biobed effluent, the herbicides bentazone (71%) and imazethapyr (64%) were also frequently detected, with a maximum concentration of 3,044 µg L^{-1} for bentazone and 51 µg L^{-1} for imazethapyr. All three herbicides—clopyralid (K_{oc}, 5 L kg^{-1}; DT_{50}, 23d; GUS, 3.02), bentazone (K_{oc}, 55L kg^{-1};DT_{50}, 20 d; GUS,1.95), and imazethapyr (K_{oc}, 52 L kg^{-1};DT_{50}, 90 d; GUS, 3.9)—might be considered somewhat environmentally mobile by water. Despite their relatively large concentrations in effluent, there was evidence that these herbicides were retained and/or degraded in the biomatrices to some extent because their mean concentrations were significantly smaller in the effluent (dual-cell bentazone 987 µg L^{-1}, imazethapyr 26 µg L^{-1}) than influent (dual-cell bentazone 3,501 µg L^{-1}, imazethapyr 66 µg L^{-1}). The exception was clopyralid, which showed numerically greater mean

TABLE 3 Pesticides detected in influent but not effluent

Pesticide[a]	Maximum concentration	K_{oc}[b]	DT_{50}[c]	GUS[d]
	μg L^{-1}	L kg^{-1}	d	
Single-cell biobeds				
Atrazine (H^1)	0.06	100 (M^1)	75 (H)	2.57 (M)
EPTC (H^1)	0.41	300 (MM)	6 (L)	2.17 (M)
Metolachlor (H^1)	0.06	120 (MM)	90 (H)	2.36 (M)
Boscalid(F)	0.05	1,040 (SM)	484 (H)	2.64 (M)
Picoxytrobin (F)	0.04	965 (MM)	24 (M)	1.35 (L)
Spiromesifen (I)	27.83	30,900 (SM)	4 (L)	−0.16 (EL)
Dual-cell biobeds				
2,4-DB (H^1)	2.46	224 (MM)	4 (L)	1.68 (L)
Benfluralin (H^1)	25.78	10,777 (SM)	120 (H)	−0.62 (EL)
Dichloprop (H^1)	0.24	74 (M^1)	10 (L)	2.39 (M)
Ethalfluralin (H^1)	2.94	6,364 (MM)	45 (M)	0.47 (L)
Fenoxaprop (H^1)	3.59	11,354 (HM)	5 (L)	0.02 (L)
MCPB (H^1)	0.3	114 (MM)	7 (L)	1.64 (L)
Oxyfluorfen (H^1)	2.65	85 (M^1)	35 (M)	0.23 (L)
Quizalofop ethyl (H^1)	29.84	540 (MM)	45 (M)	2.25 (M)
Trifluralin (H^1)	15.24	15,800 (HM)	<1 (L)	0.15 (L)
Carbaryl (I)	2.72	300 (MM)	16 (L)	2.02 (M)
Chlormephos (I)	419	1,100 (SM)	20 (M)	1.25 (L)
Cypermethrin-beta (I)	183	115,009 (I)	27 (M)	−1.52 (EL)
Cypermethrin-zeta (I)	106	44,146 (HM)	49 (M)	−1.09 (EL)
Methoprene (I)	0.45	2,535 (SM)	10 (L)	0.60 (L)
Methoxychlor (I)	1.47	80,000 (HM)	120 (H)	−1.88 (EL)
Fludioxonil (F)	8.02	145,600 (I)	164 (H)	−1.47 (EL)
Pyrimethanil (F)	1.04	535 (MM)	60 (M)	2.17 (M)
Triticonazole (F)	13.75	374 (MM)	237 (H)	2.7 (M)

Note. Pesticides indicated in italic under single-cell biobeds were detected in dual-cell biobeds influent and effluent. Pesticides indicated in italic under dual-cell biobeds were detected in single-cell biobeds influent and effluent. DT_{50}, soil pesticide half-life; GUS, Groundwater Ubiquity Score; K_{oc}, soil organic carbon coefficient. [a]2,4-DB, 2,4-dichlorophenoxybutyric acid; EPTC, S-ethyl dipropylthiocarbamate; F, fungicide; H^1, herbicide;I, insecticide; MCPB, 4-(4-Chloro-2-methylphenoxy)butanoic acid. [b]HM, hardly mobile; I, immobile;M^1, mobile; MM, moderately mobile; SM, slightly mobile. [c]H, high; L, low; M, moderate. [d]EL, extremely low; H, high; L, low; M, moderate.

concentrations in effluent (225 μgL^{-1}) than in influent (181 μgL^{-1}); however, the differences were not statistically significant.

It is possible that the materials used in the biomatrix (wheat straws, wood chips, composts, peats, soils) already contained these herbicides and that these residues became available for transport into effluent. For single-cell biobeds only, there were four active ingredients that were detected in effluent samples but never in influent samples. This included three detections of the fungicide tebuconazole (maximum concentration, 0.21 μg L^{-1}) and single detections of the fungicides metconazole (1.18 μg L^{-1}) and prothioconazole-desthio (0.02 μg L^{-1})and of the insecticide pyridaben (0.68 μg L^{-1}).In previous studies, tebuconazole, metconazole, and prothioconazole-desthio were detected as contaminants in straw and hay meant for livestock feed (Kang et al., 2016; Lin et al., 2017; Mol et al., 2014).In some biobeds, the overall concentrations of clopyralid, diclofop, fluroxypyr, or imazethapyr were greater in effluent than influent (Table 4). Both clopyralid and imazethapyr are known to be relatively persistent in some soils (O'Sullivan et al., 1998; Seefeldt et al., 2014).

The effluent of both single-cell biobeds (56%) and dual-cell biobeds (45%) had relatively large proportions of pesticides that are highly likely to be detected in biobed effluent (GUS >2.8). In contrast, the proportion of pesticides that have GUS >2.8 was only 48% in single-cell biobeds and 21% in dual-cell biobeds influent (Figure 2). Active ingredients that showed a proportionally greater presence in effluent included clopyralid (8.78–13.61% in single-cell biobeds and 3.66–8.13% in dual-cell biobeds), MCPA (3.83–6.59% in dual-cell biobeds), and imazethapyr (2.83% in influent and6.98% in effluent of the dual-cell biobeds). These active ingredients all

TABLE 4 Mean percentage reduction of concentration of four pesticides by single and dual cell biobeds

Pesticide	Single cell	Mean influent concentration	Dual cell	Mean influent concentration
	%	μg L^{-1}	%	μg L^{-1}
Clopyralid	56.67	4,508 (18)	*24.17*	181 (22)
Diclofop	*100.67*	5.87 (1)	97.92	1.71 (3)
Fluroxypyr	78.87	447 (17)	*36.91*	0.25 (3)
Imazethapyr	*2.66*	0.32 (1)	60.91	66.13 (17)

Note. Mean percentages indicated in italic were increased from influent to effluent. Numbers in parentheses refer to the number of detections of the active ingredient in influent.

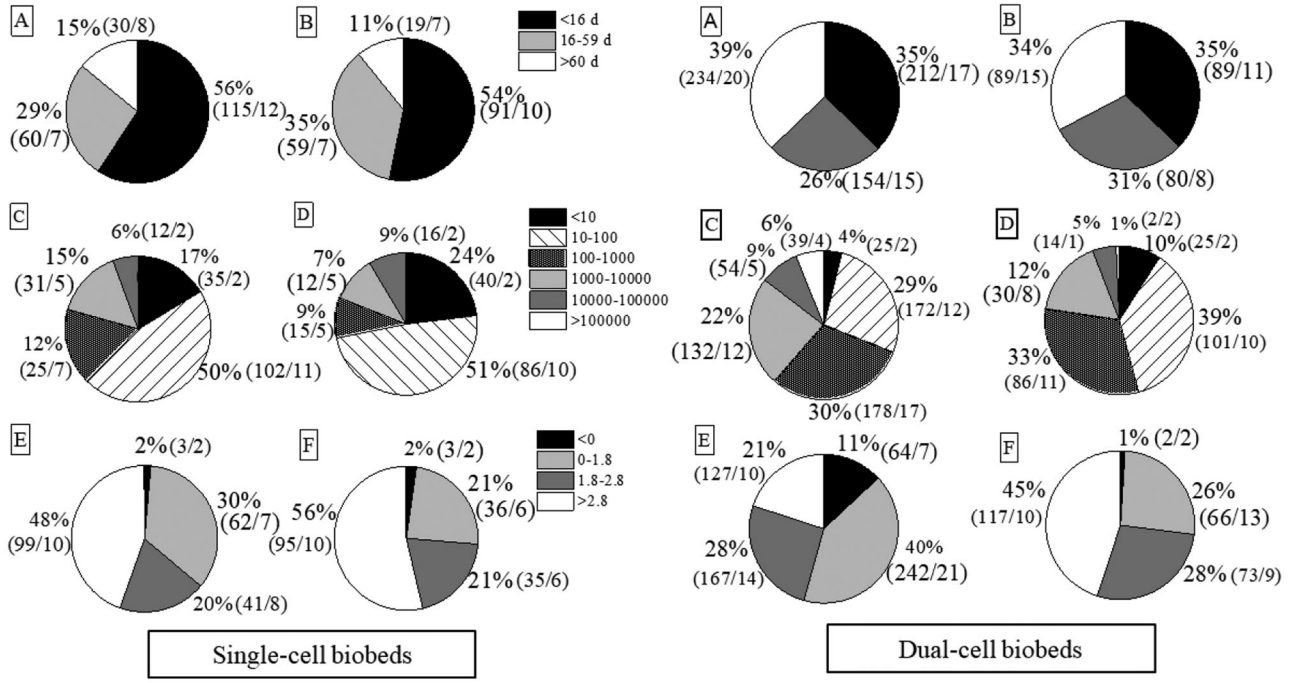

FIGURE 2 Proportional (%) detection of active ingredients by category of soil pesticide half-life values (A, influent; B, effluent), soil organic carbon coefficient values (C, influent; D, effluent), and Groundwater Ubiquity Score values (E, influent; F, effluent) for the single-cell (left) and dual-cell (right) biobeds. The numbers in parentheses refer to the total number of active ingredients detected in the category divided by the total number of unique active ingredients detected in the category

have GUS values of >2.8.Thus, overall, our results demonstrate that that our hypothesis is true because the pesticides detected in biobed effluents are more likely to be pesticides that have greater GUS values. Influent and effluent samples of both single-cell and dual-cell biobeds showed a remarkably similar distribution of DT_{50} values, and hence the proportional changes observed for GUS values were primarily driven by differences in K_{oc} values (Figure 2).

Regardless of the aquatic organism indicator, both single-cell and dual-cell biobeds influent showed significantly greater PTI values than effluent samples. Many single-cell and dual-cell biobed influent samples had PTI values >1. For example, for fish, 48% (single-cell) and 64% (dual-cell) of the influent samples had PTI >1 (Figure 3). A PTI >1 means that 50% of the indicator species die or are inhibited in their growth. The concentrations of pesticide mixtures in influent samples also resulted in a high number of influent samples showing PTI >1 for invertebrates (48 and 64%), vascular plants (88 and 75%), and nonvascular plants (88 and 71%). Despite the greater concentrations of active ingredients in the influent of single-cell than dual-cell biobeds (Figure 1), the PTI for fish and invertebrates was notably larger for dual-cell than single-cell influent (Figure 3) due to the influence of a number of active ingredients that were only detected in dual-cell biobed influent samples. This included five insecticides (chlorpyrifos, cyhalothrin lambda, cypermethrin zeta, deltamethrin, and diazinon) as well as the fungicide pyraclostrabin, which all have very low Office of Pesticide Programs aquatic life benchmarks (ranging from 0.0018 to 7.85 μgL^{-1}).

In contrast to the influent samples, both single-cell and dual-cell biobed effluent samples often had PTI <1, including

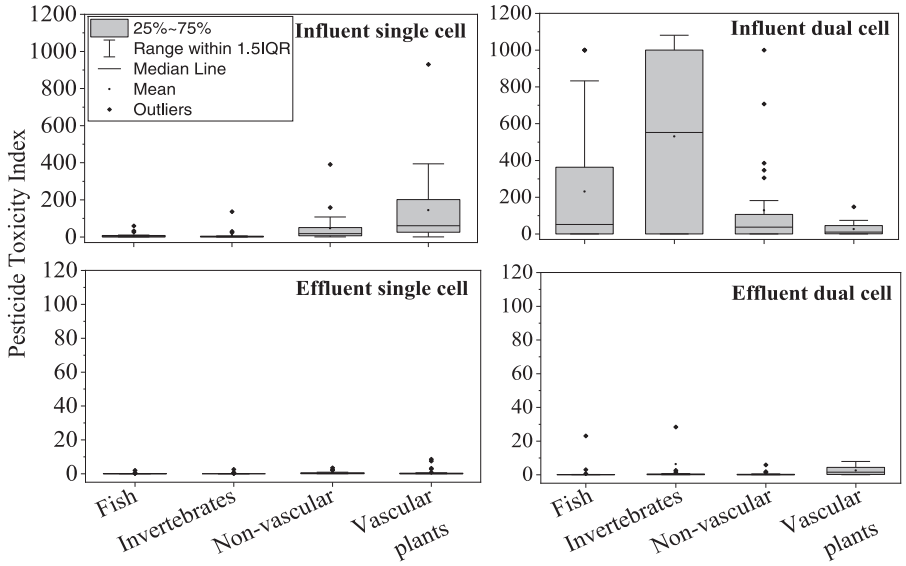

FIGURE 3 Pesticide Toxicity Index values from influent and effluent of single and dual-cell biobed for a range of aquatic organisms. IQR, interquartile range

for fish (96 and 92% of samples for single-cell and dual-cell biobed influent samples, respectively) and invertebrates (96 and 84%) as well as for vascular (84 and 40%) and nonvascular plant (88 and 88%). Given that for each of the aquatic organism indicators there was a sharp reduction in PTI values from influent to effluent samples (Figure 3), our study clearly shows that the mean PTI of biobed effluent is significantly smaller than the mean PTI of biobed influent (Figure 3). The PTI is a benchmark measure for pesticide mixtures, and hence these data again suggest that for most current-use pesticides biobeds are effective in retaining and/or degrading active ingredients. As such, the broad adoption of on-farm biobeds in the Prairies for recycling tank rinsate can become an important strategy to accelerate a green economy in North America.

4 | CONCLUSION

We conclude that biobeds are a very effective approach in colder climates for minimizing the risk of pesticides entering the broader environment. Both single-cell and dual-cell biobeds were effective for the same active ingredients by allowing for the retention and/or degradation of pesticides in biomatrices. Biobeds effectively reduced the PTI of pesticide rinsate from a value of several hundred (influent samples) to often close to zero (effluent samples). As such, our results demonstrate that the broad adoption of biobeds for recycling pesticide rinsate has potential ecological benefits. However, for some pesticides the biobeds were less effective, and further studies are required to investigate such discrepancies. This study did not include the many possible metabolites of the active ingredients measured or account for pesticide molecules binding together to form other derivatives or molecules with large molecular mass. Such efforts might require the development of more advanced analytical quantification methods.

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AUTHOR CONTRIBUTIONS

Marufa Fatema: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Resources; Software; Validation; Visualization; Writing – original draft. Annemieke Farenhorst: Conceptualization; Project administration; Supervision; Writing – review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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