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Abstract

Tile drainage and surface runoff are major pathways for pollution of water resources by agricultural nutrients and chemicals. Little is known, however, of the pathways and amounts of carbon entry into water resources from agricultural land. This paper evaluates dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) losses in tile drainage and surface runoff from a Brookston clay loam after more than a half century of monoculture maize (*Zea mays* L.), continuous bluegrass sod (*Poa Pratensis* L.), and maize-oat (*Avena sativa* L.)–alfalfa (*Medicago sativa* L.)–alfalfa rotation. Water loss in tile drainage and surface runoff accounted for 27%, 32%, and 18% of annual precipitation (876 mm) for rotation, monoculture maize, and continuous sod, respectively. Tile drainage comprised 66%–89% of water loss from rotation and continuous sod, but only 15% from monoculture maize, with the remaining 85% of water loss from monoculture maize due to surface runoff. On an annualized basis, the measured dissolved C loss was 79 and 83 kg C ha^{-1} yr^{-1}) from rotation and continuous sod, respectively, while 49 kg C ha^{-1} yr^{-1} was lost from monoculture maize. As up to 9% off-gassing loss of CO_2 from water samples was measured, total dissolved carbon losses in tile drainage and runoff water were likely greater. For Brookston clay loam soil, leaching into tile drains was the dominant mechanism for dissolved carbon loss from long-term continuous sod and crop rotation, while surface runoff was the dominant mechanism for dissolved carbon loss from long-term monoculture maize.

Key words: dissolved organic carbon, dissolved inorganic carbon, tile drainage, surface runoff, flow partitioning, cropping management

Résumé

Le drainage par canalisations en terre cuite et le ruissellement sont d'importantes sources de pollution, car l'eau achemine les oligoéléments et les composés chimiques employés en agriculture jusqu'aux réserves hydriques. On sait néanmoins peu de choses sur la quantité de carbone venant des terres cultivées qui pénètre dans les ressources hydriques, ainsi que sur les voies que cet élément emprunte pour cela. Les auteurs ont évalué la quantité de carbone organique dissous (« COD ») et de carbone inorganique dissous (« CID ») perdue par un loam argileux Brookston à cause du drainage par canalisations en terre cuite et du ruissellement après plus d'un demi-siècle de monoculture du maïs (*Zea mays* L.), de monoculture de pâturin des prés (*Poa Pratensis* L.) pour le gazonnage et d'un assolement maïs-avoine (*Avena sativa* L.)-luzerne (*Medicago sativa* L.)-luzerne. L'eau perdue en raison du système de drainage et du ruissellement correspondait respectivement à 27 %, 32 % et 18 % des précipitations annuelles (876 mm) pour l'assolement, la monoculture du maïs et la monoculture de l'herbacée. Le système de drainage explique 66 à 89 % des pertes d'eau pour l'assolement et la monoculture du gazon, mais seulement 15 % de celles relevées pour la monoculture du maïs, les 85 % restants étant attribuables au ruissellement. Ramenées à un an, les pertes de C dissous s'établissent respectivement à 79 et à 83 kg par hectare pour l'assolement et la monoculture du pâturin, la monoculture de maïs n'enregistrant des pertes annuelles que de 49 kg de C par hectare. Quoi qu'il en soit, les pertes de carbone dissous résultant du système de drainage et du ruissellement étaient sans doute plus importantes, car celles attribuées aux émissions de CO_2 par les échantillons d'eau ne s'élevaient qu'à 9 %. Le principal mécanisme à l'origine des pertes de C dissous dans le loam argileux Brookston correspond donc à la lixiviation par les tuiles en terre cuite pour la monoculture de gazon et l'assolement, et au ruissellement pour la monoculture à long terme du maïs. [Traduit par la Rédaction]

1 Introduction

Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) are important components of soil organic transformations (Kindler et al. 2011), as they affect elemental cycling and energy transfer within and between ecosystems; provide crucial resources to soil microbes; and impact the transport of heavy metals and natural contaminants between soil and surface waters (Udeigwe et al. 2011). Elevated DOC is indicative of high transfer rates of organic materials into water systems from the surrounding land area (Strock et al. 2017). Controlling DOC and DIC export from arable land is complex due to the presence of numerous carbon (C) supply and transport mechanisms, such as decomposition of soil organic matter, movement of eroded soil, subsurface tile drainage (TD), and surface runoff (SR) water. Transport of DOC and DIC in terrestrial hydrological pathways is also a key mechanism by which on-farm soil C is gained or lost (Nachimuthu and Hulugalle 2016).

Field research has shown that agricultural practices can impact both field hydrology and concentrations of dissolved C in soil and surface waters (Boyer and Groffman 1996; McTiernan et al. 2001; Dalzell et al. 2011). The concentrations of DOC in surface water vary from negligible to 36.0 mg C L^{-1} in different agricultural areas (Cronan et al. 1999; Oh et al. 2013; Bellmore et al. 2015; Strock et al. 2017; Fu et al. 2019). The majority of DOC is lost via SR (Raymond and Saiers 2010; Kindler et al. 2011; Yoon and Raymond 2012).

Different agricultural practices may affect DOC partitioning and loads. Studies have reported increasing DOC concentrations in waters from farmland relative to nonagricultural land (Mattsson et al. 2005), which might be due to larger annual fluctuations in soil moisture and temperature in farmland compared to natural land, such as forests (Don and Schulze 2008). McTiernan et al. (2001) reported a high DOC load from agricultural grasslands, and suggested it might reflect increased biomass production due to N fertilization. Intensive tillage may increase soil organic matter mineralization and DOC release, whereas no tillage is known to increase near-surface organic C content (Langdale et al. 1992; Kalbitz et al. 2000; Yang et al. 2008; Muukkonen et al. 2009; Van Eerd et al. 2014). It was found that SR flowing over organic matter rich topsoil can be an important contributor to DOC in streams (Hornberger et al. 1994; Mulholland 1997; Hagedorn et al. 2000; Manninen et al. 2018), suggesting that enrichment of near-surface soil organic matter may lead to increased DOC concentrations in SR water. Obviously, runoff water and soil contact time is a crucial factor because of the kinetic nature of DOC release from soil into water.

Water dissolved C losses are affected by discharge volume and seasonal weather conditions as well as soil type and management. Carbon losses of 25–53 kg ha^{-1} yr^{-1} were found in TD and SR from cultivated mineral soils in Finland, with slightly higher DOC concentrations coming from permanent grassland than from conventional plough or no-till arable lands, although no clear management-induced differences in the total DOC loads were observed (Manninen et al. 2018). In a surface discharge study in northern Central Valley, California, Oh et al. (2013) found annual DOC losses of 8.9–16.8 kg ha^{-1} for most agricultural watersheds, and they attributed the large range in DOC losses to differences in agricultural practices and variation in winter precipitation patterns and intensities. In a study using large lysimeters on German grasslands, Fu et al. (2019) observed annual DOC leaching losses of 6.6–27.5 kg C ha^{-1}, and found that DOC leaching was not affected by management intensity but was positively correlated with soil organic C content in the topsoil.

DIC also occurs in soil water systems, and substantial amounts of DIC are lost from forests, grasslands, and croplands via subsurface leaching (Kindler et al. 2011; Siemens et al. 2012). DIC concentrations are generally higher in carbonate rich soils than in noncarbonate soils (Jin et al. 2009; Kindler et al. 2011). Significant leaching loss of DIC occurred from carbonate-rich soils when drainage was not intercepted by plant transpiration (Amiotte-Suchet et al. 1999; Ogrinc et al. 2016). In a study on carbonate-enriched (∼5%) and C-enriched forest soil (∼14%), Schindlbacher et al. (2019) observed DIC leaching losses ranging from 200 C ha^{-1} yr^{-1} (for the control) to 390 kg C ha^{-1} yr^{-1} (for the heated and irrigated treatment). The value of 200 DIC ha^{-1} yr^{-1} loss in Schindlbacher et al. (2019) is close to the average of 180 kg DIC ha^{-1} yr^{-1} that Kindler et al. (2011) report across various land use types.

In southern Ontario, Canada, it is well established that subsurface TD and SR from agricultural fields has caused substantial nitrogen and phosphorus losses from the crop root zone, as well as serious contamination of Lakes Saint Clair and Erie (Drury et al. 1996, 2014a, 2014b; Woodley et al. 2018; Wang et al. 2018). The impacts of TD and SR on DOC and DIC losses in this region remain largely unknown, however. We consequently hypothesized that different cropping systems in the region may cause substantially different losses of DOC and DIC in TD and SR. The objective of this study was therefore to determine the effects of subsurface TD and SR on root zone losses of DOC and DIC for selected long-term agricultural practices on a widespread clay loam soil in southwestern Ontario.

2 Materials and methods

2.1 Field site and experimental design

The field site was established in 1959 at the Hon. Eugene F. Whelan Experimental Farm, Woodslee, Ontario (lat. 42°13′N, long. 82°44′W). The soil is a cool, humid Brookston clay loam (Canadian soil classification: Orthic Humic Gleysol; World Reference Base of Soil Resources: Gleysol; USDA soil classification: poorly drained, fine, loamy, mixed, mesic, Typic Argiaquoll), with the top 20 cm comprised of 280 g kg^{-1} sand, 340 g kg^{-1} silt, 380 g kg^{-1} clay, and 1.8–3.6 wt.% organic carbon depending on cropping system (Reynolds et al. 2014). The

climate is humid temperate with an average annual temperature of 8.9 °C and an average annual precipitation of 846 mm (1961–2013). The field trial is organized into 12 plots (76.2 m long × 9.2 m wide) separated by 3 m wide grass buffers, and includes 3 cropping treatments and two fertilization treatments (Fig. 1). The cropping treatments (established in 1959) included monoculture maize (MM, no replicate), continuous bluegrass sod (CS, no replicate), and a 4 yr rotation comprising maize (RM)–oat–1st yr alfalfa (Alf1)–2nd yr alfalfa (Alf2) with each crop present each year as replicates. The fertilization treatments (established in 1959) included no fertilization (other than that provided by crop residues) and annual application of synthetic fertilizer (see below for more detailed information). The above noted cropping systems were popular in 1959 when the region had a larger percentage of mixed farms with livestock. Fertilization versus no fertilization was used to produce the most extreme effects likely. However, only the data from fertilized treatments (plots 1–6) are reported here because of technical problems with the nonfertilized treatments (plots 7–12) during the experimental period. Precipitation was monitored continuously using a weather station adjacent to the field site. This study is based on data collected between May 2014 and May 2017 (56–58 years after the study was initiated), which includes three complete cropping seasons.

Maize (*Zea mays* L.) was planted at 74 500 seeds ha^{-1} using a Kinze 4 row planter (Kinze Manufacturing, Williamsburg, IA) with 76.2 cm row spacing. The fertilized treatments received granular synthetic fertilizer (16.8 kg N ha^{-1}, 29.3 kg P ha^{-1}, 27.9 kg K ha^{-1}) applied each spring as surface broadcast on alfalfa (*Medicago sativa* L.) and as surface broadcast and incorporation prior to maize and oat (*Avena sativa* L.) planting. Monoculture maize (MM) and rotation maize (RM) received an additional 112 kg N ha^{-1} as a side-dress application of injected urea-ammonium nitrate at the six-leaf stage. Herbicides were applied according to local practices to control weeds. Tillage included fall moldboard plowing (0.15–0.20 m depth) following harvest of MM, RM, and Alf2, plus spring disking and harrowing prior to maize and oat planting. Further details on the field site and agronomic practices can be found in Drury and Tan (1995), Reynolds et al. (2014), and Drury et al. (2021).

2.2 Measurement of water flows and dissolved carbon concentrations

In 1955, a single 104-mm diameter clay drainage tile was installed along the center line of each field plot at an average depth of 0.6 m. In 2007, catch basins and a heated pumping house were constructed to allow flow monitoring and sample collection and analysis of both TD water and SR water (only TD water was collected and analyzed previously). In the pump house, daily volumes of SR and TD were measured on a continuous year-round basis for each individual plot. During the growing season (May 1 – October 31), auto-samplers in the pumping house collected 1 L water samples per 1000 L of SR and per 2000 L of TD. During the nongrowing season (November 1 to April 30), the auto-samplers collected 1 L water samples per 3000 L of SR and per 5000 L of TD. The water samples were stored in sealed polypropylene bottles and

kept in darkness at 4° C until analysis. Further detail on sample collection is given in Soultani et al. (1993) and Drury et al. (2009). Analysis included vacuum filtration of the water samples through a 0.45 μm filter, and then determination of total dissolved C and DIC concentrations using a Shimadzu TOC-LCPH analyzer (Shimadzu TOC-L, Japan). The DOC concentration was determined as the difference between total dissolved C concentration and DIC concentration. Note that since the auto-sampler samples were open to the atmosphere before sealing in polypropylene bottles, DIC loss via CO_2 off-gassing may have occurred. This possibility was investigated in a supplementary laboratory study and briefly discussed below.

Cumulative water flow volume (mm), cumulative DOC and DIC loss (kg C ha^{-1}), and flow-weighted mean (FWM) C concentration (mg C L^{-1}) were determined for both TD and SR. The FWM C concentration was calculated as total C loss divided by total flow volume over a specified time period according to the FWM method of Baker and Johnson (1981). Flow volumes, FWM C concentrations, and C losses were presented on a monthly basis for each study year (i.e., 1 May 2014 to 30 April 2015; 1 May 2015 to 30 April 2016; 1 May 2016 to 30 April 2017), and also as yearly averages and 3-year totals.

2.3 Statistical analyses

The 3-year cumulative TD and SR flows and 3-year cumulative losses of DOC and DIC via TD and SR are presented without analysis of variance (ANOVA), as there were no MM and CS replicates. A SAS mixed model (SAS Institute Inc., Cary, NC, USA) was used to analyze annual volumes of TD and SR and annual losses of DOC and DIC. The data from the rotation plots were averaged to form a "rotation treatment". We did this because the TD and SR volumes and the DOC and DIC losses were not significantly different among the individual crop phases in the rotation. Consequently, annual mean was the average of 3-year single crops for MM and CS, but 12-crop-year for rotation. For rotation, an average from 4 crop phases in the same year was first taken, and then the differences in treatment mean were analyzed using year as "pseudo replicates". The analysis treated year as a repeated factor and water drainage/runoff and crop treatment as fixed factors. Least significant differences were used to compare treatment means using the LSMEANS statement ($P = 0.10$).

3 Results and discussion

3.1 Precipitation, tile drainage, and surface runoff

Cumulative precipitation varied slightly among the three "study years" (May 2014 to April 2015; May 2015 to April 2016; May 2016 to April 2017); and was 14% less than the 10-year average (876 mm) in the 2014–2015 study year (753 mm), 10% more in 2015–2016 (965 mm), and similar to the 10-year average in 2016–2017 (878 mm) (Table 1). Precipitation totals based on a May to October "cropping year" were also calculated to align with the monoculture maize and rotation (maize–oat–alfalfa–alfalfa) treatments which are planted in May with maize senescence in October. The three cropping

Fig. 1. Field plot layout and treatments at the start of measurements (2014). The plots (numbered 1–12) were separated by raised surface berms and centred longitudinally over a single tile drain (10-cm diameter, 0.7-m average depth, 12.2-m spacing). Surface runoff and tile drainage from each plot were individually routed into a central collection facility (pump house) and sampled periodically on a year-round basis. The treatments were long-term (56–58 years) monoculture maize (MM), continuous Kentucky blue grass sod (Sod), and a 4-year rotation of maize (RM) → oat (Oat) → first year alfalfa (Alf1) → second year alfalfa (Alf2). Only the results from plots 1–6 (fertilized annually) are reported in this study.
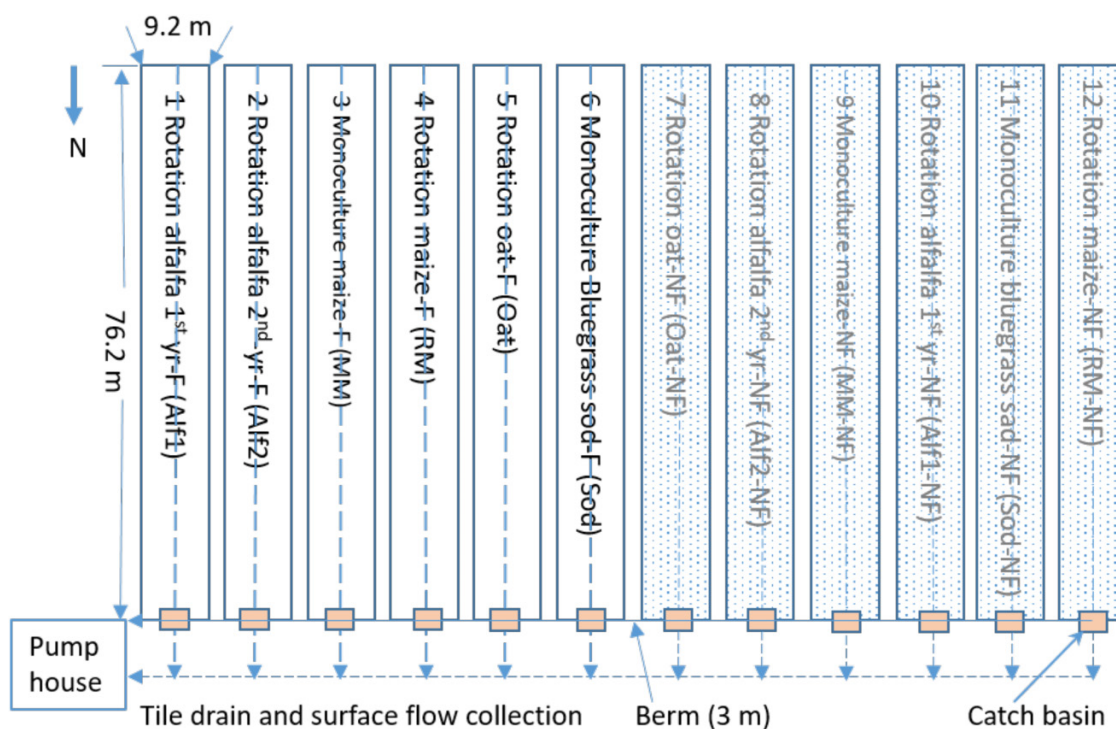
Table 1. Monthly precipitations (in mm) during study periods (2014/2015, 2015/2016, and 2016/2017) and 10-year average precipitations (2008–2017) at the experimental site.

	2014/2015	2015/2106	2016/2017	10 yr avg (2008–2017)
May	131	169	47	98
Jun	90	137	54	94
Jul	96	61	77	103
Aug	88	61	112	70
Sep	109	112	148	97
Oct	44	66	92	69
Nov	42	53	40	69
Dec	27	58	37	51
Jan	31	33	54	42
Feb	22	48	41	49
Mar	24	119	91	63
Apr	49	48	85	71
Total	753	965	878	876

year totals also varied slightly, being 5% and 14% more than the 10-year average (531 mm) in 2014 (558 mm) and 2015 (606 mm), respectively, and almost identical to the 10-year average in 2016 (530 mm). During the corresponding noncropping periods (November to April), cumulative precipitation

relative to the 10-year average (345 mm) was somewhat more variable, being 43% less than the 10 yr average in 2014–2015 (195 mm), 4% greater in 2015–2016 (359 mm), and only 1% greater in 2016–2017 (348 mm) (Table 1).

Cumulative amounts of TD and SR varied markedly among treatments over the 3-year study period. For example, TD was 105 mm for MM, 423 mm for CS, and 464–680 mm for rotation (Fig. 2b), while SR was 613 mm for MM, 53 mm for CS, and 236–344 mm for rotation (Fig. 3b). Subsurface TD and SR occurred primarily during the winter and spring nongrowing periods, which is consistent with our previous study on nitrate and water partitioning at this site (Woodley et al. 2018), as well as with a near-by Ohio study (Williams et al. 2017). The data also showed that 85% and 11% of water loss occurred as SR from MM and CS, respectively, while an average of 34% (27%–43%) was lost via SR from rotation (Table 2). Significantly less annual TD came from MM (35 mm yr^{-1}) than from CS (141 mm yr^{-1}) and rotation (185 mm yr^{-1}), while annual SR was greatest for MM (204 mm yr^{-1}), lower for rotation (94 mm yr^{-1}), and lowest for CS (18 mm yr^{-1}) (Table 2). Large differences between TD and SR were also observed from 2008 to 2013 at this site by Woodley et al. (2018), who attributed the patterns to (i) large variations in crop evapotranspiration (as evidenced by grain or alfalfa yields, Supplementary Table S1) and (ii) much larger surface (top 40 cm) soil saturated soil hydraulic conductivity (K_S) for CS and rotation (K_S = 0.04–

Fig. 2. Monthly precipitation (*a*), cumulative tile drainage (*b*), flow-weighted mean dissolved organic and inorganic carbon concentrations in tile drainage water (*c*-1 and *c*-2), and cumulative loss of dissolved organic and inorganic carbon in tile drainage (*d*-1 and *d*-2) from May 2014 to May 2017. Treatments included monoculture maize (MM), continuous Kentucky blue grass sod (CS), and a 4-year alfalfa–alfalfa–maize–oat rotation with each phase present each year (R).
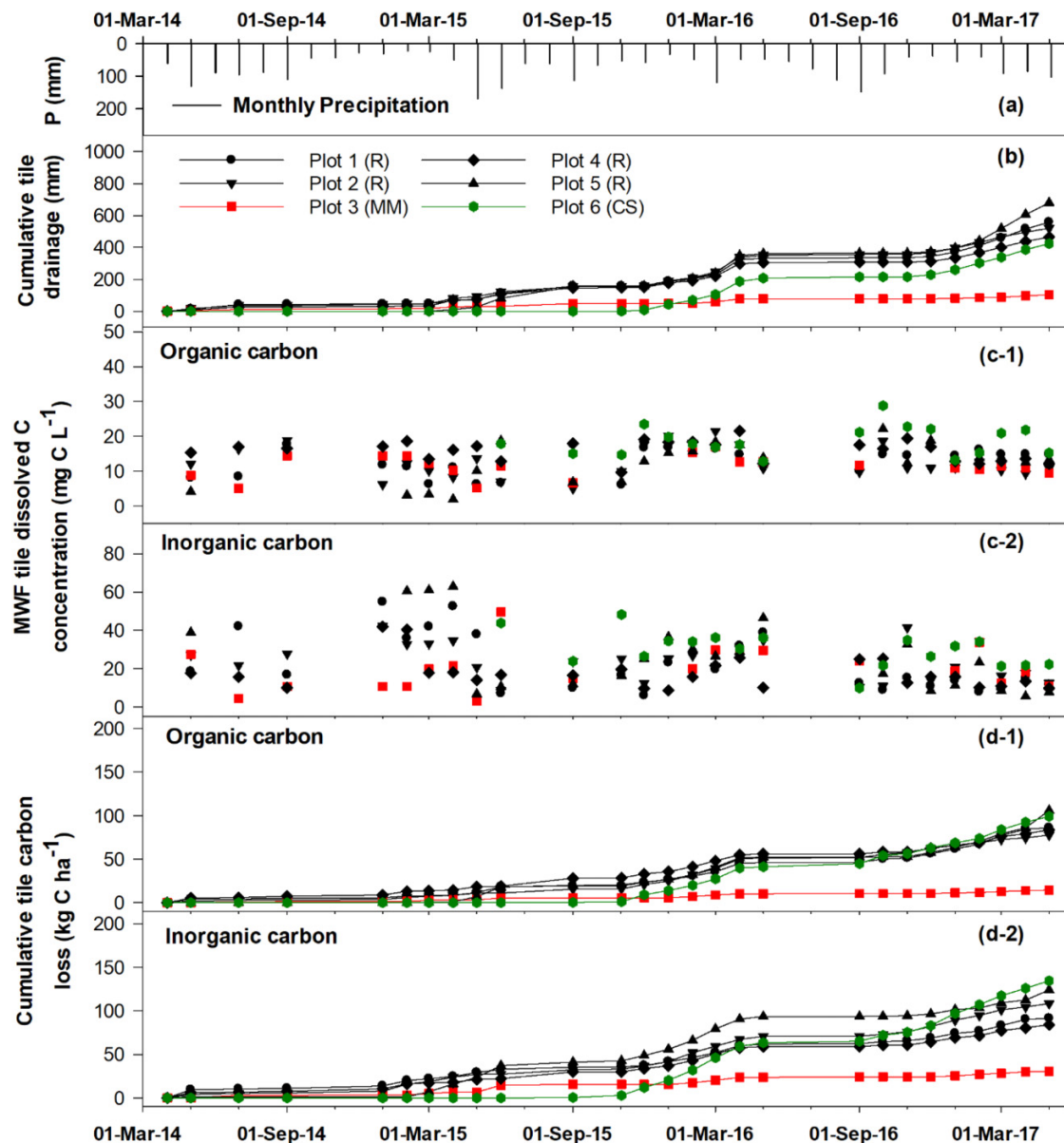
0.06 cm s^{-1}) relative to MM (K_S = 0.002 cm s^{-1}) (Reynolds et al. 2014).

3.2 Flow-weighted mean DOC and DIC concentrations

There were no clear trends in DOC or DIC concentrations among seasons, although DIC exhibited much greater variation than DOC. Over the 3-year period, average FWM C concentrations in TD were greater for DIC (22.8 mg C L^{-1}) than for DOC (13.9 mg C L^{-1}), with DIC ranging from 3.1 to 62.9 mg C L^{-1} and DOC ranging from 1.9 to 28.8 mg C L^{-1} (Fig. 4). The plotwise average FWM DOC concentrations were 11.3 mg C L^{-1} for MM, 18.7 mg C L^{-1} for CS, and 13.9 mg C L^{-1}

for rotation (12.2–15.8 mg C L^{-1}); and the corresponding plotwise FWM DIC concentrations were 20.0 mg C L^{-1} for MM, 29.9 mg C L^{-1} for CS, and 22.3 mg C L^{-1} for rotation (17.6–26.2 mg C L^{-1}) (Fig. 4).

The FWM concentrations of DOC and DIC in SR also varied over time, with greater variation for DIC than DOC, and average DIC concentration (16.9 mg C L^{-1}) greater than average DOC concentration (10.7 mg C L^{-1}) (Fig. 5). The FWM DOC concentration in runoff ranged from 3.7 to 25.7 mg C L^{-1} over the entire study period, while the corresponding FWM DIC concentration ranged from 0.8 to 57.6 mg C L^{-1} (Fig. 5). The overall average FWM DOC concentrations in runoff were 9.3 mg C L^{-1} for MM, 13.3 mg C L^{-1} for CS, and 12.2 mg C L^{-1} for rotation (10.9–14.1 mg C L^{-1}), while the overall average

Fig. 3. Monthly precipitation (*a*), cumulative surface runoff (*b*), flow-weighted mean dissolved organic and inorganic carbon concentrations in surface runoff (*c*-1 and *c*-2), and cumulative loss of dissolved organic and inorganic carbon in surface runoff (*d*-1 and *d*-2) from May 2014 to May 2017. Treatments included monoculture maize (MM), continuous Kentucky blue grass sod (CS), and a 4-year alfalfa–alfalfa–maize–oat rotation with each phase present each year (R).
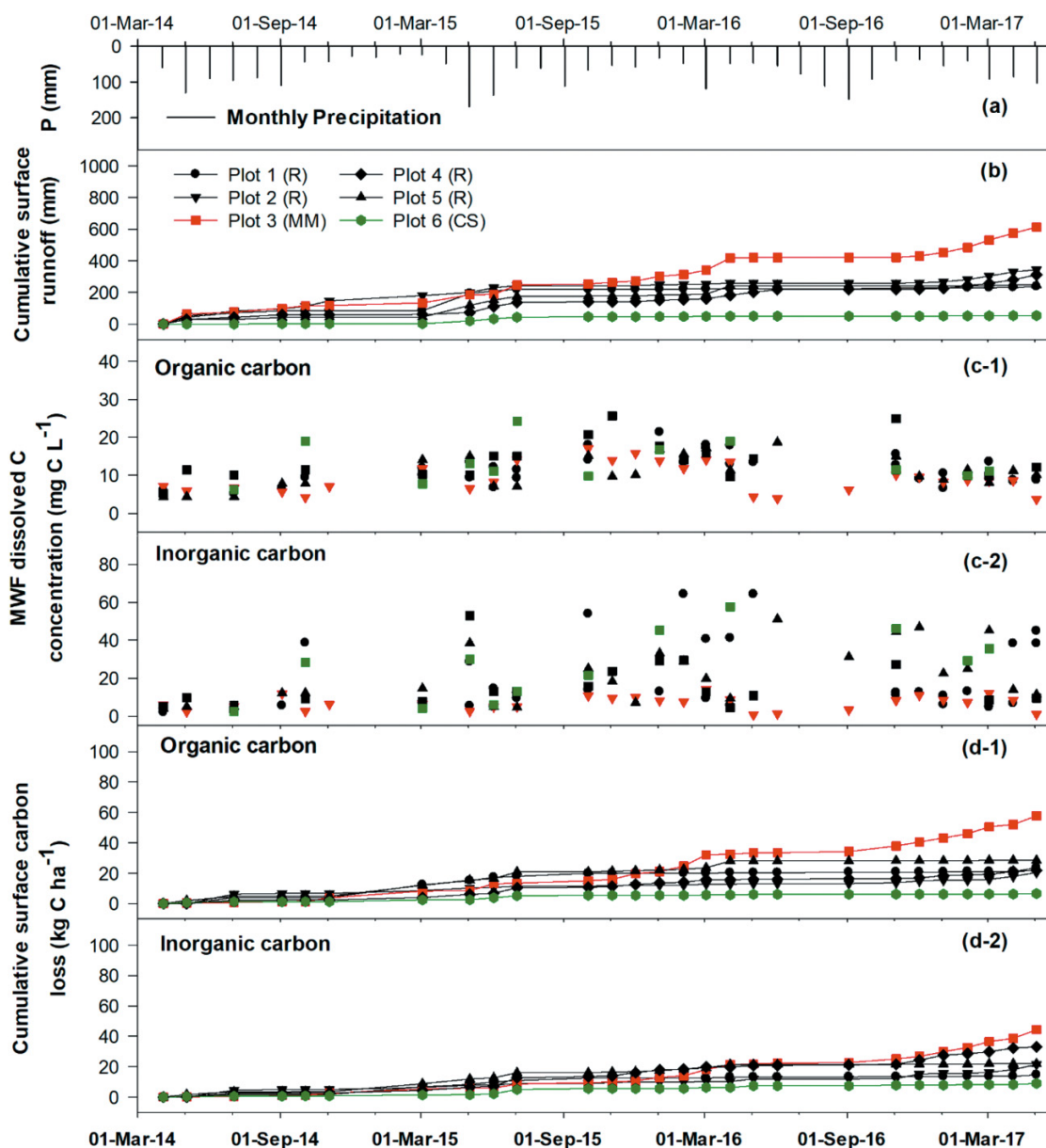
FWM DIC concentrations in runoff were 6.9 mg C L^{-1} for MM, 26.6 mg C L^{-1} for CS, and 18.6 mg C L^{-1} for rotation (16.0–21.4 mg C L^{-1}) (Fig. 5). The mean DOC concentrations and ranges were comparable to those of the Ohio study (DOC mean and range of 7.0 and 0.1–44.4 mg C L^{-1}, respectively, Williams et al. 2017), and the DOC concentrations in TD and SR fall within the DOC ranges (negligible to 36.0 mg C L^{-1}) found for agricultural areas in the US and several European countries (Cronan et al. 1999; Oh et al. 2013; Bellmore et al. 2015; Strock et al. 2017; Fu et al. 2019).

There is little information reported on DIC in SR and TD; and in addition, these data generally apply to carbonate-rich soils (Amiotte-Suchet et al. 1999; Jin et al. 2009; Ogrinc et al.

2016; Schindlbacher et al. 2019). Dissolved inorganic C is the sum of various inorganic C species, including CO_2, HCO_3^- and CO_3^{-2} (Stumm and Morgan 1996), which are produced through organic respiration, mineral weathering and mineralization of organic matter in soils and water. Hence, DIC exists not only in carbonate-rich soils but also in noncarbonate soils, such as this study where no free carbonates occur in the surface soil profile above tile depth (0.5–0.7 m). Leaching losses of both DOC and DIC are therefore important in the C balance of agricultural systems regardless of soil type and carbonate content. Fu et al. (2019) found that water-dissolved C leaching losses were positively correlated with soil organic C (SOC) in the topsoil, but not affected by management in-

Table 2. Average annual and cumulative specific volumes of tile drainage and surface runoff, loss of dissolved organic carbon, and loss of dissolved inorganic carbon from monoculture maize, continuous Kentucky blue grass sod, and a 4-year alfalfa–alfalfa–maize–oat rotation with each phase present each year.

	Monoculture maize	Rotation	Continuous sod
Cumulative specific volume (mm yr^{-1})			
TD	34.9 b B	185.2 a A	141.1 a A
SR	204.3 a A	94.3 b B	17.9 b B
Total	239.2 a	280.0 a	159.0 a
Cumulative water dissolved organic carbon loss (kg C ha yr^{-1})			
TD	4.8 b B	29.4 a A	33.0 a A
SR	19.3 a A	7.9 ab B	2.2 b B
Total	24.1 a	37.3 a	35.2 a
Cumulative water dissolved inorganic carbon loss (kg C ha yr^{-1})			
TD	10.2 b A	34.0 a A	44.8 a A
SR	14.8 a B	7.6 ab B	3.0 b B
Total	25.0 a	41.6 a	47.9 a
Cumulative total dissolved carbon (DOC + DIC) loss (kg C ha yr^{-1})			
TD	15.0 b A	63.4 a A	77.8 a A
SR	34.1 a A	15.5 ab B	5.7 b B
Total	49.1 b	78.9 a	83.5 a

Note: Means with different lower-case letters in the same row are significantly different at $P = 0.10$ level. Means with different upper-case letters in the same column under the same parameter are significantly different at $P = 0.10$.

Fig. 4. Flow-weighted mean (FWM) dissolved organic and inorganic carbon concentrations in tile drainage water collected from May 2014 to May 2017. Treatments included a first year alfalfa (Alf1), second year alfalfa (Alf2), monoculture maize (MM), rotation maize (RM), oat (Oat), and continuous Kentucky blue grass sod (CS). Boxes indicate the 25th and 75th percentile, T-bars above and below the box indicate the 90th and 10th percentile, solid dots indicate outliers, dashed lines indicate mean, and solid lines indicate median.
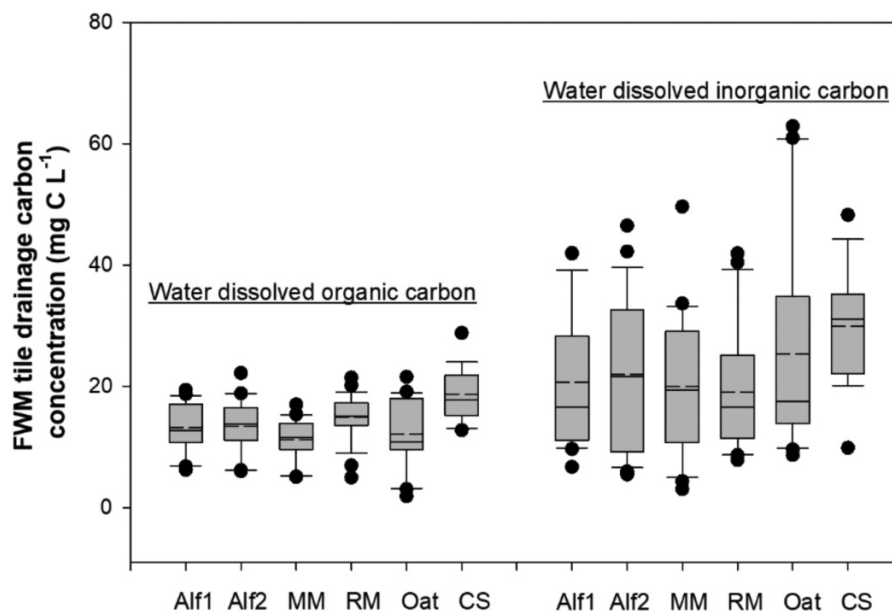

tensity. This study is consistent with Fu et al. (2019) in that CS has elevated near-surface SOC levels (SOC > 6 wt.%) relative to MM and rotation (SOC < 3.0 wt.%) (Supplementary Fig. S1).

We further found that the SR and TD waters had unexpectedly high pH values (mean ± sd = 7.83 ± 0.45, Supple-

mentary Fig. S2), which may indicate DIC loss via CO_2 off-gassing, as pH will rise as DIC/CO_2 concentration decrease. As potential DIC loss through off-gassing of CO_2 was not considered in this study, a separate assessment was conducted in a supplementary laboratory study using water samples collected in December 2021 (Supplementary Fig. S3). The supple-

Fig. 5. Flow-weighted mean (FWM) dissolved organic and inorganic carbon concentrations in surface runoff water collected from May 2014 to May 2017. Treatments included a first year alfalfa (Alf1), second year alfalfa (Alf2), monoculture maize (MM), rotation maize (RM), oat (Oat), and continuous Kentucky blue grass sod (CS). Boxes indicate the 25th and 75th percentile, T-bars above and below the box indicate the 90th and 10th percentile, solid dots indicate outliers, dashed lines indicate mean, and solid lines indicate median.
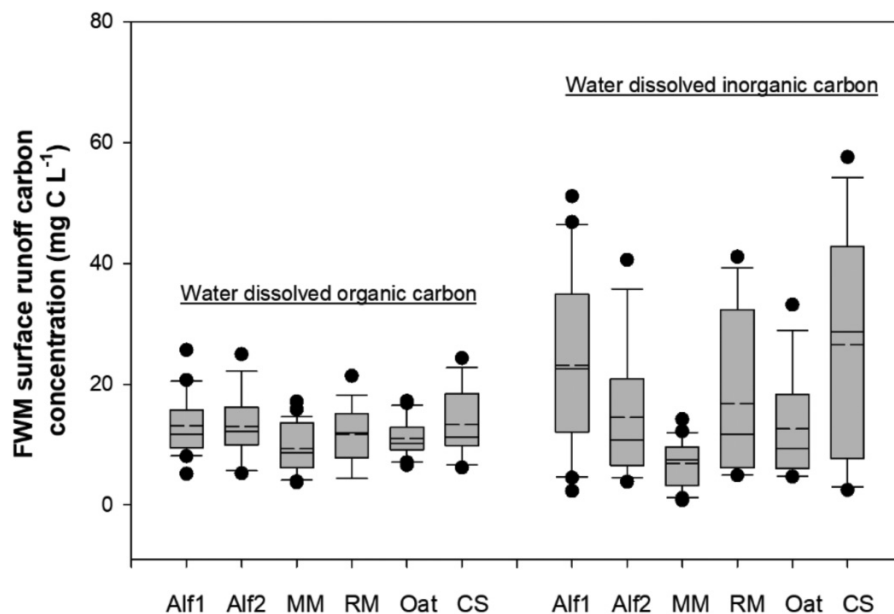
mentary study found that DIC concentrations decreased by 7.0–11.6 mg C L^{-1} after storing water samples for two weeks in partially filled containers, while DOC increased by 2.5–5.0 mg C L^{-1}. Hence, apparent off-gassing of CO_2 caused a net 6%–9% loss (5.1 to 7.4 mg C L^{-1}) in total dissolved C in the water samples. Given that our TD and runoff water samples may have also been subject to CO_2 off-gassing, the estimates given below for carbon loss may be somewhat underestimated. The DOC increase observed in the supplementary study is curious and not currently understood, but considered beyond the scope of this study.

3.3 Carbon loss in tile drainage

The cumulative DOC and DIC loss through TD was consistent with the increase in total drainage volumes (Figs. 2b, 2d-1, and 2d-2). In the winter/early spring periods from January to May of 2016 and 2017, there were large volume collections of TD water, and these resulted in larger DOC and DIC losses relative to the same periods in the previous two years (2014 and 2015) for all treatments except MM which had very little C loss. Although dissolved C loss was positively correlated with FWM DOC and DIC concentrations, higher DOC and DIC losses were due primarily to large flow volumes rather than to higher DOC and DIC concentrations. For all treatments, greater DOC and DIC tile losses in 2017 compared to 2016 were the result of more tile flow rather than higher DOC and DIC concentrations. Average annual DOC loss in tile flow was significantly lower ($P = 0.10$) from MM (4.8 kg C ha^{-1} yr^{-1}) than from rotation (29.4 kg C ha^{-1} yr^{-1}) and CS (33.0 kg C ha^{-1} yr^{-1}) (Table 2). Annual DIC loss in tile flow followed a similar pattern, with significantly lower DIC

losses ($P = 0.10$) from MM (10.2 kg C ha^{-1} yr^{-1}) than from rotation (34.0 kg C ha^{-1} yr^{-1}) and CS (44.8 kg C ha^{-1} yr^{-1}) (Table 2). Lower DOC and DIC loss from MM was due mainly to dramatically less TD and greater SR.

3.4 Carbon loss in surface runoff

Cumulative DOC and DIC loss through SR was also more strongly correlated with runoff volume than with DOC and DIC concentration (Figs. 3b, 3d-1, and 3d-2). Large runoff volumes and large runoff DOC and DIC losses occurred from March to May in 2016 and 2017 for all treatments, with large amounts coming from MM and low amounts from CS. For example, there were generally higher DIC and DOC concentrations in the SR from CS than from MM during April–June 2016, but the DIC and DOC losses were lower than MM because CS had lower SR volumes (Fig. 3d-2). Over the study period, DIC losses in SR from the rotation treatment (14.6–33.0 kg C ha^{-1} yr^{-1}) were less than those from MM (44.6 kg C ha^{-1} yr^{-1}), but significantly greater than those from CS (9.0 kg C ha^{-1} yr^{-1}) (Fig. 3). The same pattern occurred for DOC, with 20.5–28.5 kg C ha^{-1} yr^{-1} lost from rotation, 57.9 kg C ha^{-1} yr^{-1} lost from MM and 6.6 kg C ha^{-1} yr^{-1} lost from CS.

Average annual DOC losses in SR was greatest from MM (19.3 kg C ha^{-1} yr^{-1}), followed by rotation (7.9 kg C ha^{-1} yr^{-1}), and then CS (2.2 kg C ha^{-1} yr^{-1}) (Table 2). The DOC losses from MM and CS were significantly different ($P = 0.10$); however, the DOC loss from rotation was not different from either MM or CS (Table 2). Annual DIC loss in SR showed a similar pattern as DOC with significantly greater loss from MM

Fig. 6. Partitioning of total carbon loss from monoculture maize (MM), continuous Kentucky blue grass sod (CS), and an alfalfa–alfalfa–maize–oat rotation (Rotation) between: (*a*) dissolved organic and inorganic carbons; (*b*) tile drainage and surface runoff.
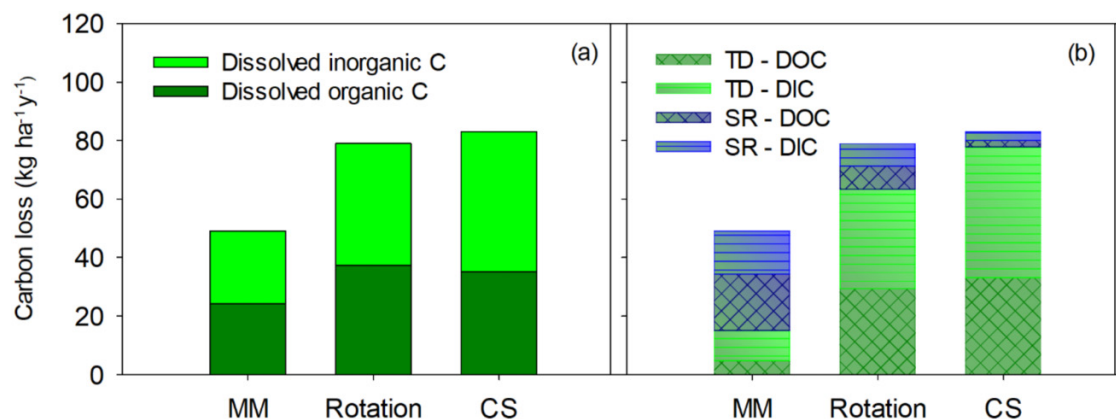
(14.8 kg C ha^{-1} yr^{-1}), followed by rotation (7.6 kg C ha^{-1} yr^{-1}), and then CS (3.0 kg C ha^{-1} yr^{-1}) (Table 2).

These results are consistent with Kindler et al. (2011) in that DOC and DIC leaching is an important aspect of C balance in agricultural systems. High DOC loss from agricultural fields should reflect vigorous biomass production (McTiernan et al. 2001). Other management practices can also affect microbial activity through modification of soil conditions, such as tillage, fertilization and liming, which have been shown to increase DOC and DIC concentrations in soil solution (Dawson and Smith 2007). Although DOC loss in SR from organic rich topsoil is often positively correlated with DOC loading to streams (Hornberger et al. 1994; Mulholland 1997; Hagedorn et al. 2000; Manninen et al. 2018), this did not occur here as more dissolved C was lost in SR from MM (which has a lower SOC concentration) than in SR from CS (which has a higher SOC concentration). By contrast, substantially more dissolved C was lost in TD from CS than from MM, suggesting that SOC enrichment may lead to increased DOC concentration in TD water.

The majority of studies on dissolved C loss from soil generally considered only DOC (Raymond and Saiers 2010; Yoon and Raymond 2012; Oh et al. 2013; Manninen et al. 2018; Fu et al. 2019); and the few studies on both DOC and DIC occurred primarily on carbonate-bearing soils (Jin et al. 2009; Kindler et al. 2011; Ogrinc et al. 2016). Our results, on the other hand, showed similar DOC and DIC losses from grain crops (both continuous maize and maize in rotation) and slightly more DIC than DOC loss from soil under long-term crop rotation and continuous sod. Although DIC losses in this study (25.0–47.9 kg C ha^{-1} yr^{-1}) were much lower than those from carbonate-rich soils (116–390 kg C ha^{-1} yr^{-1}) (e.g., Kindler et al. 2011; Schindlbacher et al. 2019), they were nonetheless substantial for a carbonate-free soil, which in turn suggests there was substantial biotic respiration and mineralization of organic matter in the crop root zone (Stumm and Morgan 1996).

and CS (83.5 kg C ha^{-1} yr^{-1}), but much lower for MM (49.1 kg C ha^{-1} yr^{-1}) (Table 2, Fig. 6). There were large differences in the partitioning of total C loss between TD and SR; on average, SR accounted for about 69.5% of total C loss from MM, but only 19.6% of total C loss from rotations, and only 6.8% of total C loss from CS (Table 2, Fig. 6).

Total DOC losses in this study (24.1–37.3 kg C ha^{-1} yr^{-1}) are substantially lower than the leaching losses of DOC (41 ± 13 kg C ha^{-1} yr^{-1}) from several cropland studies in Europe (Kindler et al. 2011), and this may be compounded by different sampling techniques used. Tile drains collected in our study were mainly water that was rather rapidly moving through the soil via large pores resulting in smaller time periods for DOC accumulation compared to suction cup technique used by Kindler et al. (2011) that extract water with a vacuum also from smaller pores in which water can accumulate higher DOC concentrations over longer periods of time. The total DOC losses are comparable to those in a Finland study (25–52 kg C ha^{-1} yr^{-1}) for cultivated mineral soils, where it was also found that management had no clear effect on DOC loads (Manninen et al. 2018). In a SR study in northern Central Valley, California, Oh et al. (2013) found annual DOC losses of 8.9–16.8 kg C ha^{-1} yr^{-1} for most agricultural watersheds, which are comparable to our result for MM (19.3 kg C ha^{-1} yr^{-1}) (Table 2). However, our DOC losses in SR from rotation and CS (7.9 and 2.2 kg C ha^{-1} yr^{-1}) were substantially lower, suggesting that DOC losses can be affected by differences in winter precipitation patterns and intensities as well as agricultural practices such as crop type and presence or absence of an over-winter cover crop (e.g., sod, alfalfa) (Table 2). Fu et al. (2019) found that the annual DOC leaching losses were between 6.6 and 27.5 kg C ha^{-1} from grasslands which are consistent with the 4.8–33.0 kg C ha^{-1} range found in this study. These results suggest that DOC leaching losses are affected strongly by topsoil organic carbon content and soil properties (especially soil permeability), which are in turn affected by soil type and management practices.

3.5 Total loss of water dissolved C (DOC + DIC)

Total annual loss of dissolved C (DOC + DIC) through TD and SR were similar for the rotation (78.9 kg C ha^{-1} yr^{-1})

4 Summary and conclusions

This study demonstrates that long-term cropping systems on clay loam soil can induce strong partitioning of water

flow and losses of dissolved organic and inorganic carbon between TD and SR. TD and SR accounted for 27%, 32%, and 19% of annual precipitation (876 mm) for rotation, monoculture maize and continuous sod, respectively; however, TD comprised 66%–89% of water loss from rotation and continuous sod, but only 15% from monoculture maize. A total of 78.9–83.5 kg C ha^{-1} loss were measured annually through TD and SR from rotation and continuous sod, while 49.1 kg C ha^{-1} loss was measured from monoculture maize. DOC accounted for less than 47% of total dissolved C loss from the rotation treatment, less than 49% from monoculture maize, and less than 42% from continuous sod. In addition, 94% and 80% of water dissolved carbon losses occurred via TD from continuous sod and rotation, respectively, but only 31% from monoculture maize. Loss of water dissolved carbon (both DOC and DIC) from this cropped clay loam soil was comparable to that found in other studies for grasslands, forests and farmlands. Considering that this study did not systematically evaluate C loss due to CO_2 off-gassing during storage and processing of water samples (estimated in a supplementary study to cause 7.5–11.6 mg C L^{-1} reduction in DIC concentrations), the actual inorganic carbon loss in the tile and SR waters could be greater than reported here.

Losses of both DOC and DIC were found to depend mainly on TD and SR volumes; and thus varied substantially among seasons, years and cropping system. Cropping and rotation significantly altered water partitioning between TD and SR, as well as DOC and DIC losses. We also found that DOC accounted for substantial amounts of total carbon loss in TD and SR for this clay loam soil. It was concluded that long-term agricultural practices can strongly influence TD, SR, and losses of dissolved organic and inorganic carbon from a Brookston clay loam soil in southwestern Ontario.

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