

# Manure and Fertilizer Effects on Carbon Balance and Organic and Inorganic Carbon Losses for an Irrigated Corn Field

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Little is known about inorganic fertilizer or manure effects on organic C (OC) and inorganic C (IC) losses from a furrow irrigated field, particularly in the context of other system C gains or losses. In 2003 and 2004, we measured dissolved organic and inorganic C (DOC, DIC) and particulate OC and IC (POC, PIC) concentrations in irrigation inflow, runoff, and percolation waters (six to seven irrigations per year); C inputs from soil amendments and crop biomass; harvested C; and gaseous C emissions from field plots cropped to silage corn (*Zea mays* L.) in southern Idaho. Annual treatments included: manure treatment (M) 13 (Year 1) and 34 (Year 2) Mg ha<sup>-1</sup> stockpiled dairy manure; inorganic fertilizer treatment (F) 78 (Year 1) and 195 (Year 2) kg N ha<sup>-1</sup> inorganic N fertilizer; or no amendment treatment (NA) as a control. The mean annual total C input was 15.7, 10.8, and 10.4 Mg ha<sup>-1</sup> for M, F, and NA, respectively, while total C outputs for the three treatments were similar, averaging 12.2 Mg ha<sup>-1</sup>. Manure plots ended each growing season with a mean net gain of 3.3 Mg C ha<sup>-1</sup> (a positive net C flux) vs. a net loss for F and NA (-1.6 and -1.5 Mg C ha<sup>-1</sup>, respectively). The C added to M was ~1.5 × that added to F or NA, yet relative to F, M increased gaseous C emissions only 1.18×, increased runoff DOC losses only 1.04×, decreased particulate runoff total C 19%, and decreased percolate DOC 32%. Increased C gas emissions from manure (relative to fertilizer) were less when silage was removed than when retained (1.18× vs. 2× reported in other studies). This suggests a means by which manure applications to corn crops can be managed to minimize C emissions. Amendments had both direct and indirect influences on individual C components, e.g., the losses of DIC and POC in runoff and DOC in percolation water, producing temporally complex outcomes, which may depend on environmental conditions external to the field.

**Abbreviations:** DIC, dissolved inorganic C; DIC<sub>r</sub>, net DIC lost in runoff; DIC<sub>p</sub>, DIC in percolate; DOC, dissolved organic C; DOC<sub>r</sub>, net DOC lost in runoff; DOC<sub>p</sub>, DOC in percolate; DOY, day-of-year; EC, electrical conductivity; ESP, exchangeable sodium percentage; F, inorganic fertilizer treatment; IC, inorganic C; M, manure treatment; NA, no amendment treatment; OC, organic C; PC, particulate C; PIC, particulate inorganic C; POC, particulate organic C; THM, trihalomethanes; TIC, total inorganic C; TOC, total organic C.

Organic C inputs to soils and crops are largely derived from photosynthesis, with atmospheric CO<sub>2</sub> being the fundamental C source (Schlesinger, 1991). Atmospheric CO<sub>2</sub> also supplies C for the formation of pedogenic IC in semiarid soil (Sahrawat, 2003). Both inorganic and organic C may also be input via irrigation water. Carbon is exported from cropped field soils in several forms: gaseous CO<sub>2</sub> released from soils during respiration, methane gas flux from soils, har-

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vested crop biomass, and dissolved or particulate C compounds in runoff or percolation water (Davidson and Janssens, 2006). The import and export of C from cropped soils is of interest because (i) they represent essential components of the net ecosystem C balance (Kindler et al., 2011), for example, soil C mineralized by microorganisms releases important amounts of CO<sub>2</sub> to the atmosphere; and (ii) soil C exported in percolation or runoff waters and entering public drinking water sources may react with added chlorine to promote formation of disinfectant byproducts such as trihalomethanes (THM) and other known carcinogens (Fleck et al., 2004). Dissolved organic C from manure added to soil as an amendment, or solubilized and leached from wastewater ponds, can increase DOC concentrations in down-gradient groundwater and tile drains and increase THM formation potential of affected water sources (Chomycia et al., 2008).

Irrigated agriculture is practiced on 299 million ha worldwide with >90% being furrow or flood irrigated (Field, 1990; International Commission on Irrigation and Drainage, 2012). Irrigation produces a large share of the total crop value in the United States, and furrow irrigation is employed on about one-third or 8.9 M ha of this acreage (USDA-National Agricultural Statistics Service, 2010). The water applied during furrow irrigation necessarily exceeds crop evapotranspiration needs (Lehrsch et al., 2005). The excess water can dissolve soil C and transport it to groundwater via deep percolation, and to natural surface waters via surface runoff and return flow (Brye et al., 2001; King et al., 2009; Ruark et al., 2010).

While much research has examined individual components of the annual C budget for agricultural soils, few studies have evaluated the entire C budget for any single system, and even fewer have also determined the effect of manure amendment on the C budget of furrow irrigated, row crop systems. Kindler et al. (2011) used porous cup samplers to collect soil percolation water at 65- or 100-cm soil depths in different forest, grassland, and cropland ecosystems across Europe to estimate DOC losses, but did not attempt to evaluate effects of manure applications in these systems. Similarly, researchers have studied DOC losses in drainage water, tile-drain, and runoff from grassland soils and corn or hay fields, but did not consider other C-budget components (Don and Schulze, 2008; Royer et al., 2007). Other studies have examined the DOC loadings in surface water inflows and runoff for furrow- or flood-irrigated fields, but did not compare untreated soils with manured soils or measure other C inputs and outputs (Poch et al., 2006; King et al., 2009; Lentz and Westermann, 2010; Mailapalli et al., 2010; Ruark et al., 2010; Krupa et al., 2012).

Little research has evaluated IC fluxes from soils, with or without manure or irrigation. However, Robbins (1986) and Heller et al. (2010) have shown that manure additions can increase CaCO<sub>3</sub> solubility and leaching in soils by increasing soil respiration and CO<sub>2</sub> partial pressures, and by increasing soil organic acid concentrations. Finlay (2003) found that DIC concentrations in surface streams can be influenced by both geochemical and biotic factors.

We hypothesized that C fluxes associated with furrow irrigated plots would differ depending on the nutrient source employed. The objective of this study on manured and non-manured calcareous soils in southern Idaho was to measure organic and inorganic C losses in irrigation runoff and in percolation waters beneath furrow irrigated corn plots and relate these to the other measured or estimated components of the system's C budget.

## MATERIALS AND METHODS

### Site and Soils

The experimental site was established in fall 2002 on furrow irrigated Portneuf silt loam (coarse-silty, mixed superactive, mesic Durinodic Xeric Haplocalcids) with 1.5% slopes near Kimberly, ID (42°31'04" N lat; 114°22'20" W long). The surface soil is a silt loam and contains on average 100 g kg<sup>-1</sup> clay, 700 g kg<sup>-1</sup> silt (hydrometer method after organic matter removal), 10 g kg<sup>-1</sup> OC (Walkley-Black), and 50 g kg<sup>-1</sup> CaCO<sub>3</sub> equivalent. The soil has a saturated-paste-extract electrical conductivity (EC) of 0.07 S m<sup>-1</sup>, an exchangeable sodium percentage (ESP) of 1.5, a pH of 7.7 (saturated paste), and a cation exchange capacity of 19 cmol<sub>c</sub> kg<sup>-1</sup> (NH<sub>4</sub>AOC method). Cropping on the site consisted of an alfalfa (*Medicago sativa* L.)–corn–bean (*Phaseolus vulgaris* L.)–grain rotation for the previous 33 yr. Between 1969 and 1986, the field received a dairy manure application (40–75 Mg ha<sup>-1</sup> dry wt.) every 3 yr, but none was applied between 1986 and 2002. In the cropping year before this study (2002), the field was fertilized with 135 kg N ha<sup>-1</sup> as urea and planted to silage corn. Plots were planted to silage corn in each season during the two year study.

We aligned the experimental plots with previously installed soil water percolation samplers (Lentz et al., 2001), which permitted us to simultaneously monitor both runoff and leaching in the soil beneath the furrows.

### Experimental Design

The experimental design was a randomized complete block with three replicates. The three treatments included (i) a control (NA, no amendments); (ii) manure (M), dairy manure applied at a locally typical rate (13 Mg ha<sup>-1</sup> dry wt. in 2003 and 34 Mg ha<sup>-1</sup> in 2004, see Field Operation section); and (iii) fertilizer (F), conventional inorganic fertilizer. We applied fertilizer N at a rate that was similar to that made available in the manure amendment (described later). Manure and fertilizer amendments are described in Table 1. Each experimental unit (i.e., plot) was 4 m wide by 57 m long and was separated from adjacent plots by a 1.3-m-wide buffer strip. Each plot included five rows of corn planted on a 0.76-m row spacing and four furrows. Every other furrow was watered in a typical irrigation event. However, due to high evapotranspiration demands in the summer of 2003, all four furrows in each plot were watered during irrigations no. 5 and 6 to maintain adequate soil moisture for the growing corn. The buffer strip included one irrigated furrow. We normally monitored and sampled runoff water from one furrow in each plot. However, on days when all four furrows per plot were irri-

**Table 1. Amendment concentrations and application rates (all on a dry wt. basis) for manure and fertilizer applied in each year of the study.**

Crop year		Application date	Stockpiled dairy manure					Form	Inorganic fertilizer				
			Concentration		Bulk application rate				Application date	Application rate			
			C	N†	Solids	C	N			Fertilizer	C	N	
			—g kg <sup>-1</sup> —		—Mg ha <sup>-1</sup> —				—kg ha <sup>-1</sup> —				
2003	Manure	10 Oct. 2002	302	18.6	13	3.92	0.242	Urea	6 May 2003	169	34	78	
2004	Manure	24 Mar. 2004	160	10.0	34	5.44	0.340	NaNO <sub>3</sub>	12 May 2004	1219	0	195	

† N = Total N.

gated, two furrows in each plot were monitored and results were reported as an average of the two.

### Soil Water Percolation Sampling

A soil water sampler was designed to continuously measure and collect percolation water draining below the 1.2-m depth in unsaturated soil. Water was collected under continuous tension from a 17-cm-long, 4-cm-diam. ceramic cup placed in the bottom of a 20-cm-diam. stainless steel container with 23-cm-high sidewalls. As the vacuum (adjusted for ambient soil conditions) was applied, the sampler intercepted both macropore and matrix-pore soil water draining through a known cross-sectional area. The percolation soil water sampler design, which produced valid measures of soil water flux rates and leachate solute concentrations was described previously along with details of the vacuum extraction system and field installation (Lentz and Kincaid, 2003). Because the percolation samplers had been installed several years prior the current study, they were well equilibrated with the field soil they monitored. During the study, the samplers were operated continuously during the growing season. These conditions ensured that adsorption/desorption reactions associated with ceramic materials did not alter soil solution DOC concentrations during collection (Beier et al., 1992; Gruggenberger and Zech, 1992; Lentz, 2006).

In each plot, three samplers were installed into the ceiling of individual cavities, which were excavated by hand into the side of a backhoe pit. The installation ensured that an undisturbed soil column extended from the soil surface downward into the interior of each sampler. The extraction vacuum set for each site was based on the tensiometer-sensed matric potential of the undisturbed soil at the top of each stainless steel container. A field-deployed vacuum pump and tank were connected via a gas dryer to a polyethylene tube main line and branch lines to each sampling site. There, vacuum was supplied via a manifold to three 1-L vacuum flasks, which collected percolation water from three individual samplers installed in each plot. These collection flasks were enclosed in an above-ground, insulated box.

### Field Operations

Details of the field operations are presented in Lentz and Lehrsch (2010). In brief, stockpiled solid manure from dairy cattle (*Bos taurus*) was applied at 13 Mg ha<sup>-1</sup> (dry wt.) to designated plots on 10 Oct. 2002 and immediately incorporated with an offset disk and roller harrow. Pre-emergence herbicide was applied to the entire area in spring 2003 and urea fertilizer

at 78 kg N ha<sup>-1</sup> was applied to designated plots on 6 May 2003. Urea is the inorganic N fertilizer most commonly used in this region to supply crop N requirements.

Silage corn was planted on 15 May 2003. The V-shaped, 0.1-m-deep furrows were formed as an integral part of the planting operation. All monitored irrigation furrows were wheel trafficked when formed in the field to reduce furrow infiltration variability. During each growing season, the field was cultivated in the first week of July to control weeds and simultaneously reshape the irrigation furrows. After silage harvest in mid-September, the remaining corn stover (15- to 30-cm-tall stems with leaves) was incorporated by disking to 0.1 m. A second manure application was made to designated plots on 24 Mar. 2004 at a rate of 34 Mg ha<sup>-1</sup> (dry wt.) and incorporated. The manure application rate was increased in 2004 for two reasons: (i) we expected that the spring manure would contain less solids and have a higher C/N ratio (due to higher straw content) than the fall manure, and (ii) the fall 2002 manure application was among the lower rates of those typically applied in the area. Pre-emergence herbicide was applied on March 31<sup>st</sup> and NaNO<sub>3</sub> fertilizer at a rate of 195 kg N ha<sup>-1</sup> was applied on 12 May 2004. The NaNO<sub>3</sub> fertilizer was derived from a Chilean source and had a unique isotopic signature, which we employed to track NO<sub>3</sub><sup>-</sup> leaching in the soils (not reported). Silage corn was planted on 13 May 2004. Other field operations in 2004 were similar to those in 2003.

### Irrigations

The Snake River water used for irrigation had an average EC of 0.04 S m<sup>-1</sup>, a sodium adsorption ratio of 0.6, and carried little sediment (<500 mg L<sup>-1</sup>). A gated pipe with adjustable spigots conveyed irrigation water across the plots at the head, or inflow-end, of the furrows. At the head of each plot, a manifold made from 0.15-m-diam. PVC pipe withdrew water from the gated pipe and directed it under equal hydrostatic pressure into each plot's irrigation furrows. After being sampled (described below), irrigation outflows from each furrow entered a tail-water ditch that ran perpendicular to the furrows at the bottom of the plots. Seven irrigations on 14-d intervals were applied to plots each year beginning on 10 June 2003 and 15 June 2004.

Irrigations began between 0730 and 0830 h and ran for 24 h. Inflows typically were set to 13.3 L min<sup>-1</sup>, which produced consistent furrow advance rates among all furrows. Furrow inflow rates, furrow stream outflow rates, and sediment (particulate) concentrations were measured during each irrigation. Outflow rates were measured and 1-L runoff water samples were collect-

ed at one-half hour intervals early in the irrigation, every hour during the mid-irrigation period, and every 2 h thereafter once irrigation outflows and sediment loads had stabilized (typically after 7 h or more into the 24-h set). Immediately after collection, each 1-L furrow runoff sample was placed in an Imhoff cone for 30 min. The volume of settled sediment was then measured and recorded. We returned two of the 1-L runoff water and sediment volumes collected from each furrow at each irrigation to the laboratory. These were filtered (Whatman no. 50) to determine sediment (particulate) mass. The two sediment volumes per furrow were specifically selected to characterize the low and high sediment-load conditions in each furrow.

We used regression functions ( $R^2 = 0.94\text{--}0.98$ ) developed for each treatment and irrigation type to determine runoff sediment concentrations from the settled sediment volumes (Lentz and Lehrs, 2010), where "irrigation type" identified furrows that were, or were not, previously irrigated. A subsample of the particulate material retained on the filter was analyzed for total C and total IC, and total OC was calculated as the difference. Approximately 11 to 12 h into the irrigation set (~1930 h, local time), a final irrigation measurement was made for the day. Monitoring was resumed at 0600 to 0730 h the next morning. The late evening and early morning readings provided a reasonably accurate mean flow and infiltration measurements for the overnight period (Lentz and Lehrs, 2010). Irrigation inflow rates were measured by timing the filling of a known volume, and outflows were measured with long-throated v-notch flumes located at the outflow end of the furrow.

## Water Sampling and Analyses

In addition to the water samples taken for sediment determinations, three to four additional runoff samples per irrigation were collected to determine dissolved C concentrations. The water was collected from v-notch flumes used to monitor runoff. Runoff C concentrations were monitored in all but the seventh (last) irrigation in 2004. Since runoff nutrient concentrations tend to be lowest in the last irrigations of the season (Lentz and Lehrs, 2010), there was little likelihood that a significant C-loss event would go unrecorded by omitting sampling in Irrigation 7. To determine the contribution of Irrigation 7 in 2004 to the cumulative constituent runoff total, we measured runoff rates during Irrigation 7 and assumed Irrigation 7 runoff concentrations were equivalent to those measured in Irrigation 6.

Previous research has shown that both sediment and other component concentrations in furrow runoff commonly peak between 1 and 3 h after furrow advance and generally declined to a lower level by 5 h after advance (Lentz et al., 2001). Therefore we collected four runoff samples per furrow during Irrigations 1 and 2 in 2003, at 5 min, 1 h, 4 h, and either 10 or 22 h after furrow advance (i.e., after runoff began). This initial sampling showed that runoff component concentrations changed little after the 4-h sampling. Thus, in the remaining irrigations in 2003 and 2004, runoff samples were collected at 5 min, 1 h, and 5 h after furrow advance. Irrigation inflow samples were also collected periodically

during irrigations to determine nutrient baseline concentrations. Samples were stabilized with a saturated  $\text{H}_3\text{BO}_3$  solution (1 mL per 100-mL sample), and a subsample was filtered through a 45- $\mu\text{m}$  Millipore membrane. Collected samples were stored at 4°C.

Two or three times per week during the irrigation season, percolation water volumes from individual samplers were collected, measured, stabilized with a saturated  $\text{H}_3\text{BO}_3$  solution, combined with previously collected water from the same samplers, and stored at 4°C. Percolation water samples contained no sediment and required no filtration. Every 5 to 14 d, the cumulative water volumes from individual percolation samplers were mixed thoroughly, and a subsample was collected and stored at 4°C until analyzed. The excess water samples were then discarded, and the process was repeated for the next period. The DOC (as non-purgeable OC) and DIC of filtered percolation and runoff water samples were determined using a Shimadzu TOC-5050A (Shimadzu Scientific Instruments, Columbia, MD).

Subsamples of the collected runoff sediment were dried and ground in a roller mill. Composited samples of the manure applied each year were subsampled to determine solids content with the remainder air dried at about 30°C. A subsample of the air-dry manure mass was ground in a Wiley mill to pass an 865- $\mu\text{m}$  screen and then freeze dried to remove moisture. We determined total particulate C (PC) in runoff sediment and manure samples using a Thermo-Finnigan FlashEA1112 CNS analyzer (CE Elantech Inc., Lakewood, NJ). Total PIC in runoff sediment samples was measured using a pressure-calculator (Sherrod et al., 2002), and total POC was determined as the difference between total PC and total PIC.

## Gaseous Carbon Fluxes

Gaseous C fluxes from the soil were estimated from in situ  $\text{CO}_2$  and  $\text{CH}_4$  emission measurements collected in 2009, 2010, and 2011 on an adjacent field with identical soil and crop, and including manure and fertilizer treatments (Lentz, unpublished data, 2014). From that study, we determined that (i) mean monthly  $\text{CO}_2\text{--C}$  gas emissions for our soils under corn were significantly correlated with mean monthly air temperatures and (ii) developed individual regression equations for predicting emissions from manured or non-manured plots. We employed these equations to estimate seasonal cumulative  $\text{CO}_2\text{--C}$  emission values for the 2 yr in the current field study, which were summed with the 3-yr seasonal mean for  $\text{CH}_4\text{--C}$  emission (Lentz, unpublished data, 2014). The  $\text{CH}_4\text{--C}$  emissions were three orders of magnitude smaller than  $\text{CO}_2\text{--C}$  emissions and poorly correlated with air temperature (Lentz, unpublished data, 2014). In the gas emission study (Lentz, unpublished data, 2014), fertilizer plots received ammonium sulfate or urea in amounts needed to meet yield targets (soil P and K levels were adequate). The manure plots received a single 42 Mg ha<sup>-1</sup> (dry wt.) manure application in fall, 2008. Supplemental inorganic-N was not added to manure plots in 2009, but was included in 2010 and 2011 to meet yield targets. A control plot was not included in the gas emission study; however, because fertilizer and

control soil treatments produce similar gas emissions (Collins et al., 2011), we assumed emissions for the two were identical in the current study.

Gas emissions were monitored between 0830 and 1130 h every week, or every other week, from late spring through fall using three 29-cm-wide by 72-cm-long by 28-cm-tall, two-piece (base and cover), static, vented chambers (Hutchinson and Livingston, 2002). The headspace in the chambers was sampled at 0, 10, 20, and 30 min after chamber placement. In 2009 the CO<sub>2</sub> and CH<sub>4</sub> concentrations in samples were measured directly in the field using a Model 1412 photoacoustic field gas monitor (Innova Air Tech Instruments, Ballerup, Denmark), and in 2010 and 2011, gas concentrations were determined by gas chromatography. Gas flux was calculated from measured changes in trace gas concentrations with time using a best-fitting statistical linear or nonlinear model. These fluxes were determined using HMR, a program package written in the R statistical language (Pedersen et al., 2010). Cumulative gas emissions across sampling dates were calculated using trapezoidal integration, assuming that measured fluxes represented average daily fluxes.

Above- and below-ground biomass C remaining after harvest (residual) and harvested corn biomass C were also measured in these gas emission plots (Lentz, unpublished data, 2014). The ratio  $B = \text{residual-biomass-C}/\text{harvested-biomass-C}$  (Lentz, unpublished data, 2014) was used in the current study to determine season-long atmospheric C uptake by the crop ( $C_{\text{Uptake}}$ ),

$$C_{\text{Uptake}} = C_{\text{Harvest}} + B(C_{\text{Harvest}}) \quad [1]$$

where  $C_{\text{Harvest}}$  = the harvested biomass C and  $B = 0.219$  for no-manure plots and 0.265 for manure plots (Lentz, unpublished data, 2014).

## Calculations and Statistical Analysis

The inorganic fertilizer amounts added in 2003 and 2004 were intended to supply an N-rate equivalent to the supplied manure's available N. Since the manure analysis had not been completed before fertilizer application, we calculated the available N from manure assuming that the manure's total N equaled 1.5% of the total manure dry mass and that 40% of the manure total N became available during the growing season. These quantities represented averages for manures in south-central Idaho (A. Leytem, personal communication, 2002). Subsequent chemical analyses verified that the manures we applied each year contained an average 1.4% total N (Table 1; Lentz and Lehrs, 2010).

The computer program WASHOUT calculated sediment and C loads in furrow stream outflows, flow-weighted component concentration means for individual furrows, and integrated component losses over the duration of the irrigation. A more detailed description of these determinations was presented by Lentz and Lehrs (2010). In brief, the inflow and outflow rates, and runoff sediment volumes, and masses for selected samples were input to the program. It develops regression functions relating runoff settled sediment volume to sediment mass ( $R^2 = 0.94$

to 0.98), using them to convert runoff sediment volume values to mass before calculating the outputs. The runoff DOC and DIC were similarly calculated except that no conversion function was required. Net runoff DOC and DIC concentrations and losses were calculated by subtracting the inflow C concentration from the runoff C concentration before input into WASHOUT. These values are denoted by DOC<sub>n</sub> and DIC<sub>n</sub>, where the n subscript signifies "net."

The POC and PIC runoff concentrations and loads for a given furrow were computed by multiplying the furrow runoff sediment concentration or load values (derived from WASHOUT) by the average concentrations of POC or PIC in the sediment (determined on a per year, irrigation, and treatment basis). Because inflow total particulate C concentrations were negligible, the net and gross values for POC, PIC, and total PC were equivalent. Thus, the computed DOC<sub>n</sub>, DIC<sub>n</sub>, and particulate runoff C concentrations and mass-loss values reflect only the effect of treatments, and are not influenced by inflow C concentrations.

The DOC and DIC of percolation waters were computed on a gross basis only because the total dissolved C concentration of water infiltrating into furrows above percolation samplers was not known (and was not necessarily equivalent to that of inflow waters). Mean runoff sediment and C concentrations (i.e., flow-weighted means) for a given furrow and irrigation were computed as the ratio of total mass loss divided by total outflow volume. The percolation dissolved C concentrations were also calculated as flow-weighted means. Season-long cumulative values for irrigation parameters (furrow inflow and infiltration volumes) and component inputs and losses were also computed.

Data from each irrigation in 2003 and 2004 were analyzed via ANOVA, PROC Mixed (SAS Institute, 2009) using a repeated measures approach, which accounted for correlations among the values of response variables measured from one irrigation to the next. The model included treatment, year, and irrigation as fixed effects, and block with its associated interactions as random effects. Response variables (runoff C concentrations and losses for individual irrigations) were transformed using common Log or square root to stabilize variances and improve normality. The LSmeans and 95% confidence intervals were back transformed to original units for reporting. An ANOVA on season-long cumulative values was performed using PROC Mixed to determine the effect of treatment and year on each parameter. The model included treatment and year as fixed effects with block and its associated interactions as random effects. No transformation of the raw data was needed to analyze season-long cumulative values. All analyses were conducted using a  $P = 0.05$  significance level.

## RESULTS

Water applied via irrigation in 2003 and 2004 comprised 84 and 86% of the total received by the plots. Natural precipitation contributed the remaining percentage, but was not observed to have produced runoff at the site (Lentz and Lehrs, 2010). Both 2003 and 2004 were dryer than normal. Precipitation for the 8 mo before June, 168 mm in 2003 and 167 mm in 2004, was less

**Table 2. The influence of nutrient treatment, irrigation number, and year on furrow hydraulic parameters and net runoff sediment, dissolved and particulate C concentrations and cumulative losses in irrigation furrow runoff. Table gives *P*-values for main effects and interactions in an analysis of variance.**

Source of variation	<i>P</i> -values														
	Furrow hydraulic parameters†			Mean irrigation runoff concentrations						Cum. mass losses in each irrigation					
	Inflow	Infilt.	Outflow rate	Dissolved		Particulate				Dissolved		Particulate			
			DOC	DIC	Sed	POC	PIC	Tot PC	DOC	DIC	Sed	POC	PIC	Tot PC	
Treatment (TRT)	0.7	0.7	0.7	0.3	0.2	0.4	0.7	0.8	0.4	0.3	0.3	0.4	0.9	0.8	0.8
Irrigation number (IRR)	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***
Year (Y)	***	0.2	***	***	***	0.1	0.5	0.1	0.2	***	***	*	0.2	*	*
TRT × IRR	0.6	0.9	0.8	0.3	0.3	0.07	***	0.1	*	0.3	0.1	*	***	0.1	*
TRT × Y	0.4	0.5	0.3	0.2	0.4	0.1	0.2	0.2	0.3	0.09	0.1	0.2	0.2	0.3	0.3
IRR × Y	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***
TRT × IRR × Y	0.8	0.2	0.1	0.09	**	*	0.3	0.2	*	0.08	***	*	0.08	0.1	0.07

\* Significant at the 0.05 probability level.

\*\* Significant at the 0.01 probability level.

\*\*\* Significant at the 0.001 probability level.

† Infilt. = infiltration; DOC = dissolved organic C; DIC = dissolved inorganic C; Sed = sediment; POC = particulate organic C; PIC = particulate inorganic C; Tot PC = total particulate C.

than the mean value recorded for either the 1996 to 2011 (208 mm) or 1960 to 1990 (205 mm) periods, and was among the driest reported from 1996 through 2011. The mean air temperature in 2003 (10.3°C) was warmer than that recorded during either the 1996 to 2011 (9.3°C) or the 1960 to 1990 (8.4°C) periods, and warmer than that observed for 2004 (9.2°C). Specifically, the mean air temperatures for the 2002 to 2003 winter and July–August periods were 2.2°C warmer than the corresponding periods for 2004.

The ANOVA results reported in Tables 2 and 3 examined data for individual irrigations across both years. Treatment had no significant influence on furrow hydraulic parameters, neither as a main effect nor in interaction with irrigation number or year (Table 2). Treatment was not significant as a main effect but interacted with irrigation, year, or both to influence net runoff sediment, DIC, POC, Total PC concentration and losses (Table 2), and cumulative DOC losses in percolation water (Table 3). Furthermore, the irrigation-by-year interaction was significant, indicating that the pattern of flow and net runoff

C concentrations and losses observed among irrigations varied between years (Table 2). The same was true for percolation water parameters (Table 3).

### Furrow Inflows and Infiltration

Furrow inflows typically contributed about 220 mm of irrigation water (in gross) per set (Table 4). Furrow inflows did not differ among treatments (Table 2). Hence, any observed treatment effects on C parameters for a given year and irrigation were a result of the treatments themselves, not inflow conditions (Table 2). Furrow infiltration was also unaffected by treatment (Table 2). However, it did vary among irrigations from year to year, mainly in response to differences in furrow stream wetted perimeter, flow velocity, and maximum sediment concentration (Trout, 1992; Trout et al., 1995). The overall effect of treatment on irrigation runoff (outflow) rate was not significant (Table 2). However, in the first four irrigations of 2004 the mean outflow rate for manure exceeded those for control or fertilizer furrows, with the difference being significant for Irrigation 3, where manure outflow was 1.3 times that for the control (Fig. 1).

### Particulates in the Furrow Stream

Particulate concentrations in irrigation inflows were too small to measure. Hence, inflow POC and PIC concentrations were assumed to be negligible. The overall mean sediment concentration in furrow runoff was 2950 mg L<sup>-1</sup>, compared to 31 mg L<sup>-1</sup> for POC and 48 mg L<sup>-1</sup> for PIC (Fig. 2, Table 4). The seasonal pattern of cumulative sediment, total PC, and POC runoff losses was consistent across both years, with peak losses occurring in the second or third irrigation (Fig. 2). Cumulative particulate mass losses for a given irrigation generally did not differ among treatments (Fig. 2). However, in irrigation two the fertilizer and control treatments consistently produced two to three times greater runoff sediment, total PC, and POC than the manure treatment (Fig. 2).

**Table 3. The influence of nutrient treatment, irrigation number, and year on percolation water parameters: cumulative volume; gross dissolved organic and inorganic C concentrations; and cumulative losses. Table gives *P*-values for main effects and interactions in an analysis of variance.**

	<i>P</i> -Values				
	Cumulative percolation	Concentration †		Cum. losses	
		DOC	DIC	DOC	DIC
Treatment (TRT)	0.3	0.4	0.2	0.7	0.6
Irrigation number (IRR)	***	**	**	**	***
Year (Y)	0.1	0.5	0.07	0.8	0.3
TRT × IRR	0.9	0.9	0.9	0.9	0.4
TRT × Y	0.6	0.4	0.2	0.2	0.4
IRR × Y	***	***	***	***	***
TRT × IRR × Y	0.9	0.9	0.9	0.9	0.4

\*\* Significant at the 0.01 probability level.

\*\*\* Significant at the 0.001 probability level.

† DOC = dissolved organic C; DIC = dissolved inorganic C.

**Table 4. Effect of year by irrigation number on furrow hydraulic parameters, net runoff concentrations, and cumulative losses (on per furrow basis) for sediment and particulate inorganic C (PIC), and gross percolation water dissolved organic C (DOC<sub>p</sub>) and dissolved inorganic C (DIC<sub>p</sub>) concentrations and cumulative losses. Data have been averaged across treatments.**

Parameter †	2003 irrigations							2004 irrigations						
	1	2	3	4	5	6	7	1	2	3	4	5	6	7
	Runoff													
Furrow inflow, mm	250 b‡	168 d	221 c	226 c	220 c	215 c	220 c	223 c	220c	230 c	227 c	278 a	222 c	221 c
Furrow infiltration, mm	92 a	49 cd	73 b	66 bc	86 ab	68 bc	57 c	43 d	48 cd	55 cd	65 bc	84 ab	62 bc	58 c
Outflow rate, L min <sup>-1</sup>	9.5 b	6.9 d	9.0 bc	9.6 b	8.0 c	8.4 c	9.7 ab	10.8 a	10.3 ab	10.1 ab	9.5 b	9.4 b	9.7 b	9.8 b
Sed. conc., g L <sup>-1</sup>	3.6 bc	5.3 ab	4.3 bc	3.8 bc	0.1 e	1.1 d	1.3 d	2.5 c	4.0 bc	6.5 a	4.5 b	2.9 c	1.7 d	1.1 d
Sed. loss, Mg ha <sup>-1</sup>	5.5 bc	6.5 ab	6.3 bc	6.0 bc	0.1 e	1.6 d	2.1 d	4.5 c	6.6 bc	11.5 a	7.1 b	5.6 c	2.8 d	1.8d
PIC conc., mg L <sup>-1</sup>	62 bc	99 ab	76 b	66 b	1 c	18 c	22 c	47 bc	80 b	127 a	82 b	33 c	32 c	20 c
PIC loss, kg ha <sup>-1</sup>	96 bc	120 b	111 bc	107 bc	2 d	27 c	36 c	84 bc	134 b	225 a	131 b	67 c	52 c	33 c
	Percolation Water													
Cumulative percolation, mm	0.4 d	0.9 cd	0.9 cd	0.5 cd	4.7 bc	32.2 a	49.7 a	4.1 bc	10.4 b	5.4 bc	0.7 cd	0.2 d	1.4 cd	2.3 c
DOC <sub>p</sub> conc., mg L <sup>-1</sup>	0.8 cd	2.0 cd	1.2 cd	0.4 d	4.4 abc	9.0 b	11.1 a	7.4 ab	5.9 ab	6.5 ab	1.2 cd	0.2 d	3.5 c	4.7 abc
DOC <sub>p</sub> Loss, kg ha <sup>-1</sup>	0.2 c	0.2 c	0.3 c	0.2 c	1.3 bc	4.0 ab	6.3 a	3.0 b	4.9 ab	2.5 bc	0.5 c	0.1 c	1.0 c	1.1 bc
DIC <sub>p</sub> conc., mg L <sup>-1</sup>	0.8 cd	1.7 cd	1.2 cd	0.6 d	6.1 abc	12.0 b	15.5 a	11.1 b	12.4 b	12.5 b	2.6 cd	0.2 d	4.5 c	7.5 abc
DIC <sub>p</sub> Loss, kg ha <sup>-1</sup>	0.4 d	0.4 d	0.8 d	0.8 d	4.4 cd	13.3 b	19.0 a	6.7 c	10.6 bc	5.6 cd	1.4 d	0.1 d	2.2 d	3.6 cd

† Sed. = sediment in runoff; PIC = particulate inorganic C in runoff; DOC<sub>p</sub> = gross dissolved organic C in percolate; DIC<sub>p</sub> = gross dissolved inorganic C in percolate.

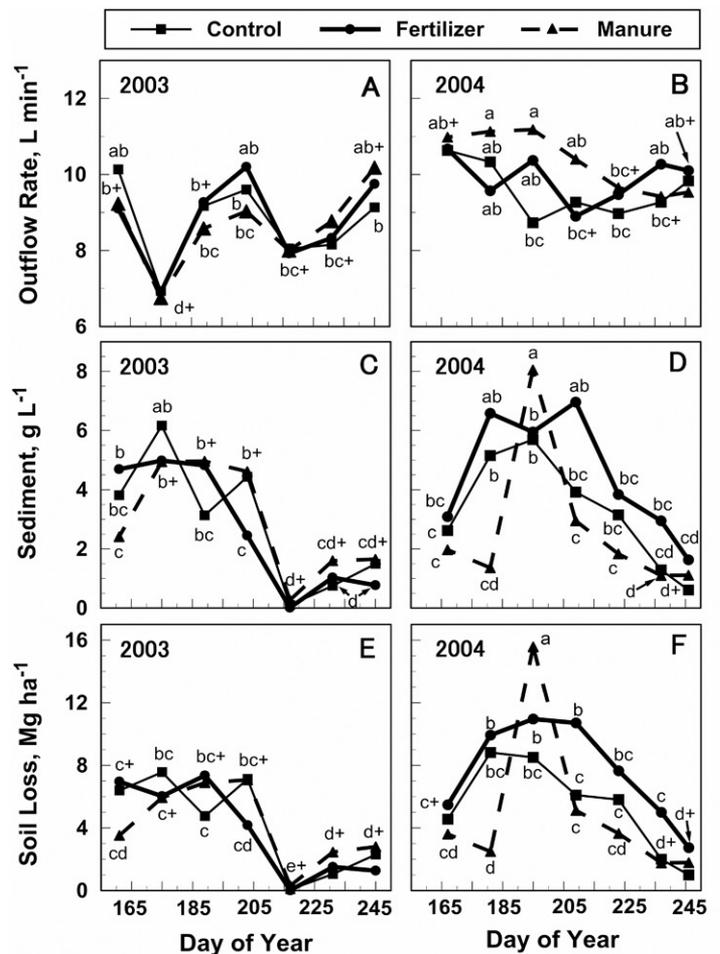
‡ For a given parameter (row), individual year-by-irrigation means followed by the same letter are not significantly different ( $P < 0.05$ ).

The irrigation runoff sediment concentrations and cumulative sediment losses were influenced by a common, significant interaction between treatment, irrigation, and year (Table 2). All treatments produced similar runoff sediment concentrations and mass losses in 2003 irrigations; however, in 2004, the fertilizer treatment often produced greater runoff sediment values than did the manure treatment, with the control producing intermediate values (Fig. 1C–1F). This occurred even though manure furrows tended to have greater mean outflow rates than fertilizer furrows in 2004 (Fig. 1B).

In each irrigation each year, the three treatments generally produced similar runoff concentrations for POC, Total PC (Fig. 3E–3H), and PIC (data not shown). However, significant differences among treatments occurred in some irrigations. For both runoff POC and total PC concentrations on day-of-year (DOY) 204 in 2003, control and manure treatments exceeded that of the fertilizer, and on DOY 181 in 2004, fertilizer exceeded that of manure, with the control being intermediate (Fig. 3E–3H).

### Furrow Dissolved Organic Carbon and Dissolved Inorganic Carbon Concentrations

The average DOC concentration in irrigation inflows was 9.7 mg L<sup>-1</sup> in 2003 and 5.8 mg L<sup>-1</sup> in 2004 (Fig. 4A and 4B). Similarly, the inflow DIC was 22.7 mg L<sup>-1</sup> in 2003 and 24.5 mg L<sup>-1</sup> in 2004 (data not shown in tabular format). Thus, the variation from year to year for DOC was nearly twice that for DIC. When averaged across all treatments, the mean annual gross runoff (or outflow) DOC concentrations were 11.6 mg L<sup>-1</sup> in 2003 and 6.1 mg L<sup>-1</sup> in 2004, while gross runoff DIC was 27.0 mg L<sup>-1</sup> in 2003 and 25.1 mg L<sup>-1</sup> in 2004 (Fig. 4C and 4D).



**Fig. 1. Furrow outflow rate (A, B), runoff sediment concentration (C, D), and sediment losses (E, F) as affected by year (2003 on left vs. 2004 on the right), irrigation, and treatment. Values are derived from irrigation means. Treatment-by-irrigation-by-year means are significantly different at  $P < 0.05$  if labeled with a different letter [plus (+) symbol following letters indicates adjacent means within an irrigation are identically labeled].**

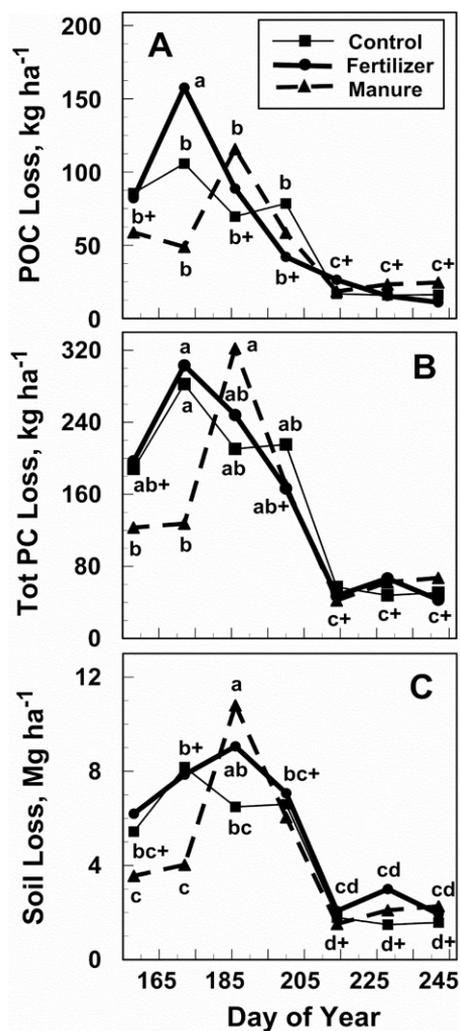


Fig. 2. Runoff particulate organic C (POC) (A), total particulate carbon (PC) (B), and sediment (C) losses for each treatment and irrigation, averaged across years. Treatment-by-irrigation means are significantly different at  $P < 0.05$  if labeled with different letters (+ symbol following letters indicates adjacent means within an irrigation are identically labeled).

Both the DOC and DIC concentrations in water exiting the furrows (i.e., outflows) typically exceeded that of the inflowing water. On average in 2003, runoff DOC and DIC concentrations were 1.2 times that of inflow values (Fig. 4A and 4C) while in 2004 they were 1.04 times greater than inflow values (Fig. 4B and 4D). The increase in furrow outflow DOC over inflow (i.e.,  $DOC_n$ ) was greatest when inflow DOC concentrations were greatest, that is, in 2003 when, presumably, conditions were more favorable for DOC production in field soils (Fig. 3A and 3C). In 2003, the runoff  $DOC_n$  concentrations per irrigation ranged from 0.1 to 6.2 mg L<sup>-1</sup>, peaking at midseason (Fig. 3A). The mean annual runoff  $DOC_n$  concentration in 2003 was 2.6 mg L<sup>-1</sup> for the control, 2.4 mg L<sup>-1</sup> for manure, and 1.8 mg L<sup>-1</sup> for fertilizer, but differences were not significant and no trend in treatment effects was discernible.

In 2004, the mean runoff  $DOC_n$  concentrations for irrigations were low and varied little among irrigations (Fig. 3B). The manure  $DOC_n$  concentrations were equal to or greater than the

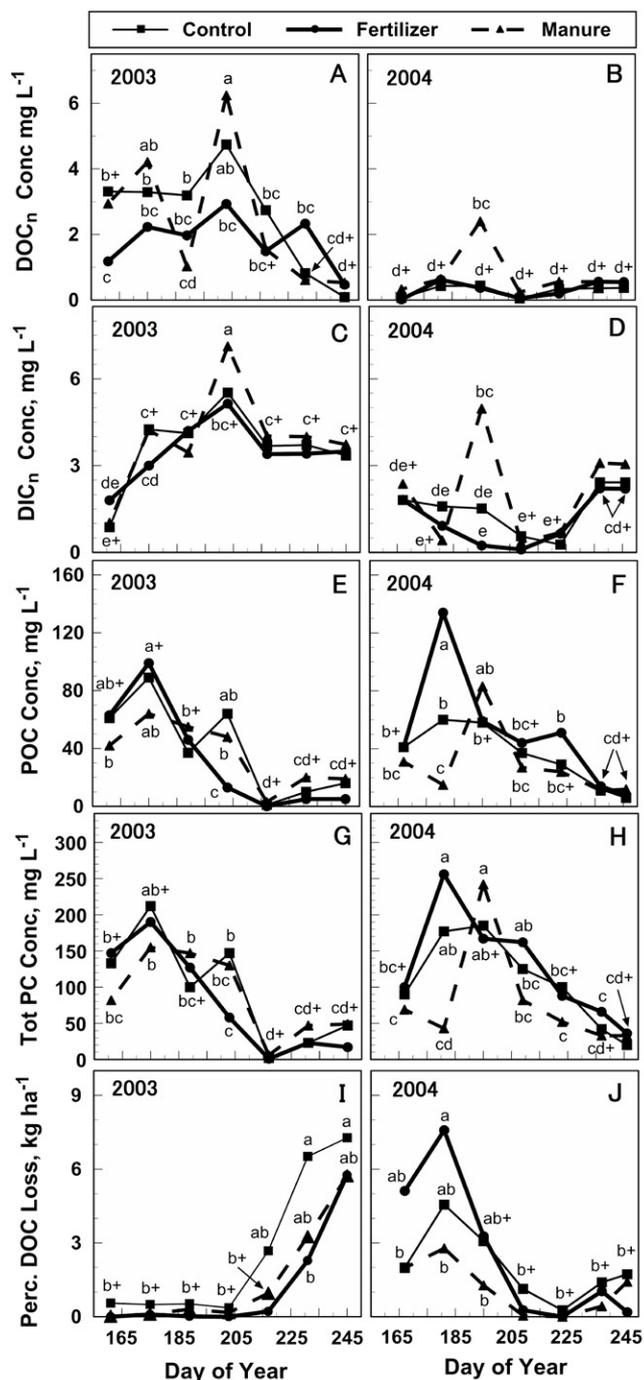


Fig. 3. Net dissolved organic C ( $DOC_n$ ) concentration (A, B), net dissolved inorganic C ( $DIC_n$ ) concentration (C, D), particulate organic C (POC) concentration (E, F), total particulate C (PC) concentration (G, H) in furrow runoff, and dissolved organic C (DOC) losses in percolation water (I, J) by year (2003 on left vs. 2004 on the right), irrigation, and treatment. Treatment-by-irrigation-by-year means are significantly different at  $P < 0.05$  if labeled with a different letter (+ symbol following letters indicates adjacent means within an irrigation are identically labeled).

control and fertilizer values; the manure means exceeded the control in six of seven irrigations in 2004, but differences were significant only in Irrigation 3 (Fig. 3B). In 2004, the mean annual  $DOC_n$  concentration for manure was 0.8 mg L<sup>-1</sup> compared to the control and fertilizer mean (0.3 mg L<sup>-1</sup>). This suggested

that the spring 2004 34-Mg ha<sup>-1</sup> manure application had a small, but more consistent influence on net runoff DOC concentrations in following irrigations than did the 13 Mg ha<sup>-1</sup> manure applied in the fall of 2002.

In 2003, both net runoff DOC (DOC<sub>n</sub>) and sediment concentrations were greatest earlier in the season and least at season's end (Fig. 3A and 1C). On an irrigation to irrigation basis, however, there appeared to be little parallelism between the two (Fig. 3A and 1C). In 2004, a relationship between DOC<sub>n</sub> and sediment concentration was not evident, except for the abrupt spike observed in both concentrations for manured plots on DOY 195 (Irrigation 3) (Fig. 1D and 3B).

The runoff DIC<sub>n</sub> concentrations across irrigations (Fig. 3C and 3D) revealed a similar pattern to that of DOC<sub>n</sub> (Fig. 3A and 3B). During the 2003 irrigation season, the DIC<sub>n</sub> increased to a maximum in Irrigation 4, then declined, while in 2004 the runoff DIC<sub>n</sub> remained relatively flat across irrigations, except for the manure treatment, which attained an abrupt maximum in the third irrigation.

### Runoff Dissolved Organic Carbon and Dissolved Inorganic Carbon Mass Losses

The pattern of DOC<sub>n</sub> and DIC<sub>n</sub> runoff concentrations observed for each irrigation (Fig. 3A–3D) closely paralleled that for the net cumulative dissolved C mass losses, so the graphs of the C losses were not shown. For the seven irrigations each year, the overall DOC<sub>n</sub> mass losses (on a per furrow basis) in 2003 averaged 3.2 kg ha<sup>-1</sup> irrigation<sup>-1</sup> (range: 0.1–9.4) and in 2004 averaged 0.74 kg ha<sup>-1</sup> irrigation<sup>-1</sup> (range: 0.1–4.7). The overall DIC<sub>n</sub> mass losses averaged 5.5 kg ha<sup>-1</sup> irrigation<sup>-1</sup> in 2003 (range: 1.4–10.6) and 2.8 kg ha<sup>-1</sup> irrigation<sup>-1</sup> in 2004 (range: 0.2–9.4).

### Dissolved Organic Carbon and Dissolved Inorganic Carbon in Percolation Water

When averaged across treatments, cumulative percolation volume at the 1.2-m depth ranged from 0.2 to 49.7 mm per irrigation (Table 4) with a total of 89.3 mm lost during the 2003 growing season, or 18% of infiltrated irrigation water vs. 24.5 mm in 2004, or 6% of infiltrated irrigation water. These values were substantially lower than the average 135 mm reported for these plots in 1997 and 1998 (Lentz et al., 2001), for which pre-season precipitation amounts were 1.6 times greater than in the current study.

For the 2 wk following each irrigation in 2003 and 2004, (i) percolation volumes varied between 0 and 124 mm, (ii) percolation flow-weighted mean DOC concentrations ranged from 1.1 to 62.7 mg L<sup>-1</sup>, and (iii) percolation flow-weighted mean DIC concentrations ranged from 2.9 to 56.4 mg L<sup>-1</sup>. Effects on percolation DOC mass losses depended on the year and irrigation (Table 3). The mean percolation DOC losses for manure plots were equal to or less than the control (Fig. 3I and 3J). Treatments as a main effect did not significantly in-

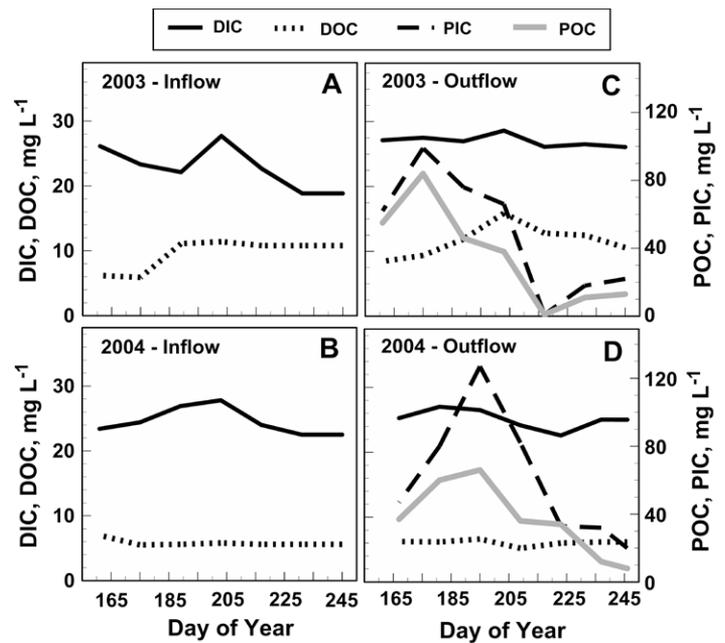


Fig. 4. Gross furrow dissolved organic C (DOC) and dissolved inorganic C (DIC) concentrations for inflows in 2003 (A) and 2004 (B), and gross DOC, DIC, particulate organic carbon (POC), and particulate inorganic carbon (PIC) concentrations in furrow outflows for 2003 (C) and 2004 (D) by irrigation. The outflow concentrations are averaged across treatments and calculated as flow-weighted means.

fluence cumulative percolation volumes or DOC and DIC concentrations and cumulative mass losses during the post-irrigation intervals (Table 3). However, these parameters were significantly affected by irrigation-by-year interactions (Table 3), which are shown in Table 4. Cumulative percolation losses in the 2 wk after an irrigation were greatest either early or late in the irrigation season, when estimated actual evapotranspiration (ET) losses were minimal. In 2003 the greatest DOC and DIC losses in percolation occurred after Irrigation 5 when the number of furrows irrigated per plot was doubled to meet unusually high crop transpiration demands in late July and August. In 2004, the maximum percolation losses of DOC and DIC occurred in early summer (Irrigations 1, 2, and 3; Table 4).

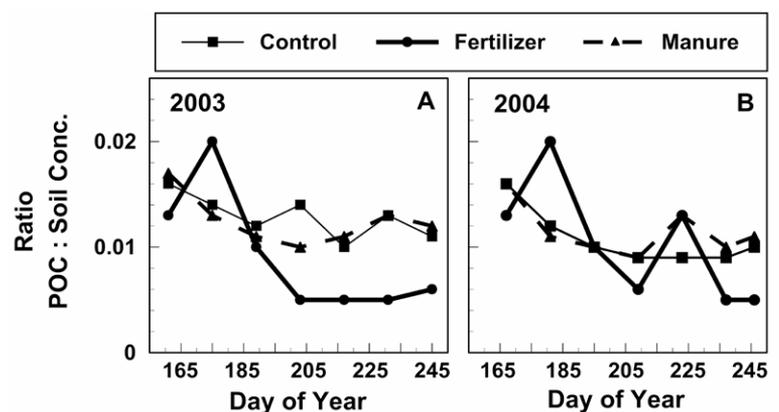


Fig. 5. Ratio of runoff particulate organic C (POC) concentration to runoff sediment concentration as a function of treatment and irrigation in 2003 (A) and 2004 (B).

**Table 5. Cumulative gross seasonal C inputs and losses in the furrow-irrigated, calcareous soil and silage corn crop by treatment and year, including the 2-yr mean.**

Treatment	Year	C Inputs†				C Outputs (losses)										Net C flux‡		
		Fert/manure		CO <sub>2</sub> uptake into biomass		Total C inputs		Irrigation runoff		Percolation		Soil C gas emissions		Biomass removal			Total C Outputs	
		C	DOC	DIC	DOC	DIC	DOC	DIC	DOC	DIC	DOC	DIC	CO <sub>2</sub> -C	CH <sub>4</sub> -C	C		C	kg ha <sup>-1</sup>
Control	2003	0	151ab§	352b	10856	11359b	126a	285b	1172	19	69	2220	2220	8913	12803	-1444b		
		34	149b	346b	10306	10835b	119a	285ab	849	8	22	2220	2220	8461	11965	-1130b		
		3920	152a	352b	11699	15123a	119a	287ab	906	11	32	2700	2700	9331	13364	2729a		
	2004	0	98c	398a	8875	9371b	69c	289ab	1270	14	45	2160	2160	7287	11136	-1765b		
		0	98c	398a	10172	10668b	72bc	295ab	1555	19	29	2160	2160	8352	12482	-1814b		
		5440	97c	396a	9296	15230a	80b	327a	1036	8	24	2450	2450	7398	11323	3906a		
2003	-	124	350	10954	12773	122	286	971	12.5	41	2380	2380	8895	12711	62			
	-	97	397	9448	11756	74	304	975	14.0	33	2260	2260	7679	11647	109			
2004	2-yr	-	124	375	9866	10364b	97	287	1221	16.5	58	2190	2190	8100	11970	-1605b		
		-	123	372	10239	10752b	96	290	1202	13.8	25	2190	2190	8407	12223	-1472b		
		-	125	374	10498	15677a	100	307	971	9.4	28	2575	2575	8354	12344	3333a		

† DOC = dissolved organic carbon; DIC = dissolved inorganic carbon; PIC = particulate inorganic carbon; POC, particulate organic carbon.

‡ Change of C in system, calculated as input C minus output C. Positive values signify a net gain in system C.

§ For a given comparison category, means in the same column followed by the same letter are not significantly different ( $P < 0.05$ ).

## Annual Carbon Flux

The mean annual total C input into manure plots was 15.7 Mg ha<sup>-1</sup> yr<sup>-1</sup>, 1.5 times greater than that for control or fertilizer while total C outputs for the three treatments were similar, averaging 12.2 Mg ha<sup>-1</sup> yr<sup>-1</sup> (Table 5, Fig. 6 and 7). Thus, the manure plots ended each growing season with an average net gain of 3.3 Mg C ha<sup>-1</sup> (a positive net C flux). Manure applied to this soil acts as a C sink, although presumably a portion of the manure-C is only temporarily stored, eventually being cycled back to the atmosphere. The non-manure treatments finished the season with a net C loss, a net C flux of -1.6 Mg C ha<sup>-1</sup> yr<sup>-1</sup> for the control, and -1.5 Mg C ha<sup>-1</sup> yr<sup>-1</sup> for the fertilizer; therefore, these treatments represented a C source. In comparison to the control treatment, manure amendments produced greater seasonal C losses for soil C gas emissions (Lentz, unpublished data, 2014) and runoff DOC in 2004. On the other hand, mean C losses for particulate C in runoff and DOC and DIC in percolation water trended lower for manure than for the control.

The greatest source of input C by far was atmospheric CO<sub>2</sub> incorporated into the crop biomass, comprising 95% of the mean annual total C contributed to control and fertilizer plots and 67% of that for manure plots (Fig. 6 and 7). The dairy manure contributed an average 31% of total C input each year to manure plots while 4% of the total C input to all plots came from irrigation water inflows of DOC and DIC. The C input to soils in rainfall was estimated from an analysis of June rainfall samples collected locally and seasonal patterns reported by Likens et al. (1983). June rainfall total OC concentrations averaged 3.55 mg L<sup>-1</sup> while total IC concentrations were below detection limits. Assuming that non-growing season rainfall DOC concentration was half that of the June sampling (Likens et al., 1983), we estimated the annual rainfall C contributions in Fig. 6 and 7 to be less than 0.006 Mg ha<sup>-1</sup> yr<sup>-1</sup>.

Of the average seasonal total C losses that had occurred by the end of the growing season (i.e., outputs averaged across years and treatments in Table 5), aboveground crop biomass removed 68% while soil gas emissions accounted for 19%, particulate runoff C 9%, dissolved runoff C 3%, and dissolved, percolation water C 0.4%. The cumulative DOC and DIC losses in percolation water were not influenced by treatment or year ( $P > 0.44$ ). The mean annual DOC leached from these soils was 13.2 kg ha<sup>-1</sup> yr<sup>-1</sup> and the DIC leached was 37 kg ha<sup>-1</sup> yr<sup>-1</sup> (Table 5). The cumulative gross total organic C (TOC) (DOC + POC) losses in runoff did not vary with treatment or year ( $P > 0.88$ ) and, overall, averaged 443 kg ha<sup>-1</sup> yr<sup>-1</sup>. The cumulative gross total inorganic C (TIC) (DIC + PIC) losses in runoff also were unaffected by treatment or year ( $P > 0.34$ ). The gross TIC losses in runoff averaged 723 kg ha<sup>-1</sup> yr<sup>-1</sup>.

Some treatment effects, year effects, or both, were observed in the cumulative C input and C output responses (Table 5). The total seasonal DOC inputs via irrigation water inflows were (i) greater for manure than fertilizer plots in 2003 (152 vs. 149 kg ha<sup>-1</sup>) because inflow rates happened to be slightly

greater in the former plots compared with the latter and (ii) less in 2004 compared with 2003 because of decreased irrigation water DOC concentrations in 2004. The total DIC inputs via irrigation water inflows were greater in 2004 compared to 2003 because inflow rates and DIC concentrations were slightly greater in 2004 (Table 4). Treatment influenced annual C losses only for runoff DOC in 2004 where manure runoff DOC exceeded that of the control by 11 kg ha<sup>-1</sup>, a 1.16-fold difference (Table 5).

## DISCUSSION

All furrow flow and C concentration and loss responses were influenced by irrigation number and irrigation-by-year interactions (Table 2 and 3). These effects illustrate the dynamic nature of the C system and were likely the result of seasonal and year-to-year variations in precipitation, irrigation, or infiltration rates; variable C inputs in irrigation water; or by effects of fall vs. spring manure application. Some of these factors are considered in more detail in the following paragraphs with regard to specific C parameters.

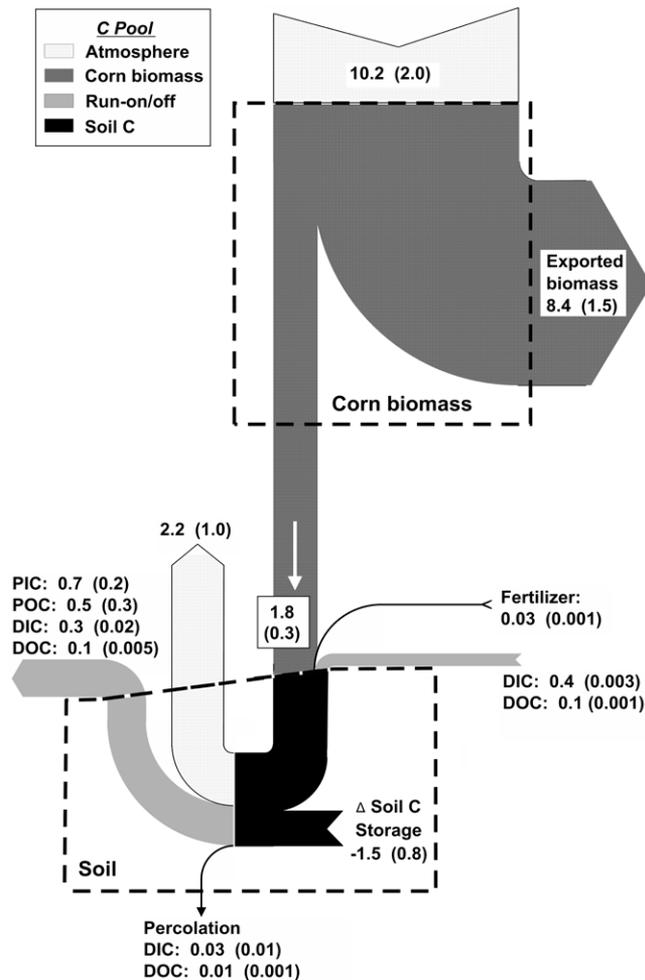


Fig. 6. Mean annual transfers of C in Mg C ha<sup>-1</sup> into and out of an irrigated silage corn and calcareous soil system amended with inorganic fertilizer. The value shown in parentheses is the standard error of the mean ( $n = 8$ ). DIC, dissolved inorganic C; DOC, dissolved organic C; PIC, particulate inorganic C; POC, particulate organic C.

## Runoff Sediment and Particulate Carbon

Sediment and particulate organic and inorganic C concentrations observed in furrow runoff were far greater than those found in natural surface waters. Relative to river water in agricultural watersheds, furrow stream concentrations values were 2- to 86-fold greater for sediment (Borah et al., 2003) and 18 to 28 times greater for POC (Kronholm and Capel, 2012). The average sediment concentration in furrow runoff, 2.7 g L<sup>-1</sup>, was 150-fold greater than the suspended sediment concentration measured in the Snake R., which receives this irrigation return flow (C. Robison, personal communication, 2012). Part of this difference is because the furrow stream measurement includes bed load whereas the river measurement does not.

## Manure and Fertilizer Effects on Runoff Sediment

In 2004, the fertilizer treatment often produced greater runoff sediment concentrations and mass losses than did the manure treatment (Fig. 1C–1F). We attribute this result to the manure's ability to increase soil aggregate stability (Nyamangara et al., 2001; Wortmann and Shapiro, 2007) and, in fertilizer furrows, to the effects of increased Na from the 2004 NaNO<sub>3</sub>-N application,

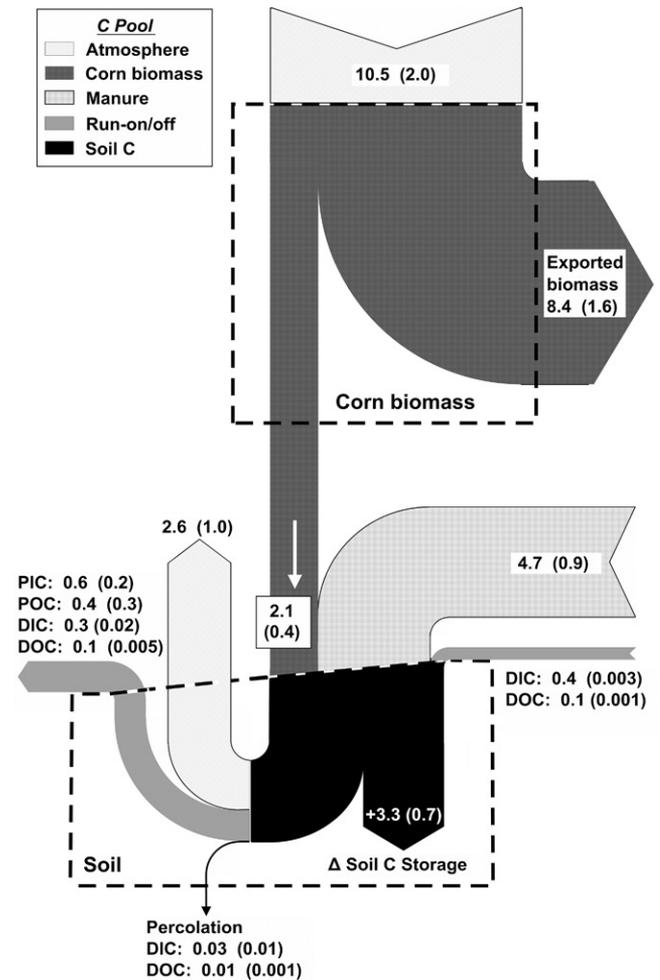


Fig. 7. Mean annual transfers of C in Mg C ha<sup>-1</sup> into and out of an irrigated silage corn and calcareous soil amended with stockpiled dairy manure. The value shown in parentheses is the standard error of the mean ( $n = 8$ ). DIC, dissolved inorganic C; DOC, dissolved organic C; PIC, particulate inorganic C; POC, particulate organic C.

which potentially increased the surface soil's Na concentration by  $\sim 10 \text{ mmol}_c \text{ Na kg}^{-1} \text{ soil}$ . Also, nearly three times as much manure was applied in 2004, greatly increasing the soil stabilizing effects of manure in 2004 surface soil. In the fertilizer furrows, the increased Na potentially increased soil exchangeable Na and hence soil dispersion, leading to decreased soil aggregate stability and increased furrow erosion relative to manure furrows (Goldberg et al., 1988; Levy and Torrento, 1995; Li and Zhang, 2010).

The apparent protection provided by the manure in 2004 temporarily and inexplicably broke down on DOY 195, Irrigation 3, causing a spike in erosion, which resulted in manure runoff sediment losses that were twice that of the control (Fig. 1D and 1F). This was accompanied by a similar spike in runoff DOC, DIC, POC, and total PC concentrations (Fig. 3B, 3D, 3F, and 3H) as well as dissolved  $\text{NO}_3^-$ , ammonium, orthophosphate, Ca, and K loads (Lentz and Lehrsch, 2010). The outflow rate and, hence, the erosive power of the manure-treated furrow stream in Irrigation 3 was only slightly higher than that of the previous irrigation (Fig. 1B), so the reason for the erosion spike is unclear. It is possible that all the relatively loose soil present in the manure furrows that had not been eroded in the previous two irrigations was flushed out in Irrigation 3, owing to the manure's waning stabilizing influence.

### The Relationship between Runoff Sediment and Particulate Carbon

The particulate organic and inorganic C concentrations and cumulative losses generally paralleled their respective sediment concentration and loss patterns (Fig. 1C, 1D, and 3E–3H; Table 4). A similar POC-sediment relationship was reported by Strickland et al. (2012) and Wu et al. (2004). The notable exception to this in the current study was the fertilizer treatment, where changes in runoff POC losses often did not correspond well with sediment losses. For example, when averaged across both years, a 1.3-fold increase in fertilizer runoff sediment losses from Irrigation 2 to 3 (Fig. 2C) produced a 1.9-fold increase in POC (Fig. 2A); a 1.2-fold increase in fertilizer runoff sediment loss between Irrigations 2 and 3 (Fig. 2C) produced a 44% decrease in POC (Fig. 2A). The former case resulted from an abrupt increase in the proportion of POC in the fertilizer runoff sediment from Irrigation 1 to 2 and the latter from an abrupt decrease in the fertilizer POC-sediment ratio from Irrigation 2 to 3 (Fig. 5A). Similarly, on DOY 195, 209, and 223 in 2004 (Irrigations 3, 4, and 5) the lack of positive relationship between fertilizer POC runoff concentrations (Fig. 3F) and runoff sediment concentration (Fig. 1D) was caused by an abrupt decrease in the runoff POC-sediment ratio from Irrigation 3 to 4, followed by an abrupt increase in the ratio between Irrigations 4 and 5 (Fig. 5B).

Conversely, the PIC data closely paralleled sediment responses throughout the experiment (data not shown). This evidence supports the concept that PIC is present in soil as free particles of varying sizes or precipitated on soil particles without regards to particle size whereas POC, in addition to occurring as

free colloids (Dalzell et al., 2011), is preferentially bound to soil clays. Thus, erosion and transport processes in the furrow stream may potentially enrich POC concentrations, but not PIC, by selectively increasing sediment clay fractions.

For manure, changes in runoff PC concentrations were primarily attributed to the manure's influence on sediment concentrations. In contrast, runoff PC concentrations in fertilizer furrows in the first irrigations of the season appeared to be controlled by other factors in addition to runoff sediment concentrations. The transient and dissipating nature of these additional controlling factors suggests that temporary changes in soil solution chemistry caused by fertilizer amendments altered the relative POC content in the eroded sediment. The increased  $\text{NH}_4^+$  and  $\text{Na}^+$  concentrations (Fox et al., 1952; Levy and Torrento, 1995; Haynes and Naidu, 1998) or changing pH (Suarez et al., 1984) in fertilized soils may have increased soil dispersion and decreased aggregate stability, which in turn increased the proportion of finer, POC-rich particles present in the eroded sediment (Wu et al., 2004). In addition, the fertilizer could have altered the quantity of OC carried by soil particles. By changing ionic strength or pH in soils, the fertilizer may have influenced the DOC adsorption or desorption characteristics of soil particles (Hope et al., 1994; Kalbitz et al., 2000).

### Dissolved Carbon in Irrigation Water

The DOC concentration in local irrigation water inflows typically varies from year to year, ranging between 2 and  $13 \text{ mg L}^{-1}$  (Lentz, unpublished data, 2013). The greater inflow DOC concentrations in 2003 may be related to the unusually warm 2003 summer temperatures, which intensified soil drying between wetting events (Kalbitz et al., 2000; Dalzell et al., 2007).

### Gross Dissolved Organic Carbon Concentrations in Furrow Runoff

The mean gross DOC concentration of furrow runoff in 2003 ( $11.6 \text{ mg L}^{-1}$ ) was similar to the  $12.7 \text{ mg L}^{-1}$  reported in rainfall runoff from corn plots in Quebec, Canada (Royer et al., 2007). This Canadian study did not assess the year to year variability in runoff DOC.

### Net Dissolved Organic Carbon Lost in Furrow Runoff

The DOC concentration in irrigation water increased as it traversed the field, producing positive  $\text{DOC}_n$  values. The runoff  $\text{DOC}_n$  concentrations in the current study (Fig. 3A and 3B) were 18 to 33% of the  $34.8 \text{ mg L}^{-1}$  concentration reported by Lentz and Westermann (2010) in runoff from a recently manured Portneuf soil. In the Lentz and Westermann (2010) study, (i) the manure had been incorporated into dry soil (water contents  $< 0.05 \text{ g g}^{-1}$ ) just 2 wk before the irrigation, and (ii) little or no microbial activity or leaching had occurred in the manured soil before the irrigation. Thus, water soluble C concentrations in their manured soil were high. However, when Lentz and Westermann (2010) delayed the irrigation on the manured soil

until the following spring, the runoff  $\text{DOC}_n$  concentration in the first irrigation averaged only  $2.4 \text{ mg L}^{-1}$ . This suggests that the manure-derived DOC was easily leached from the surface soil and/or was rapidly metabolized by soil microbes (Chantigny, 2003) and likely explains why the current study did not identify definitive and consistent treatment, and particularly manure, effects on runoff  $\text{DOC}_n$  and  $\text{DIC}_n$  concentrations and losses.

On the other hand, in the current study, the average  $\text{DOC}_n$  in furrow runoff was greater in 2003 than in 2004, regardless of treatment (Fig. 3A and 3B). This result was contrary to our expectation, particularly for the manure treatment, because the amount of manure added in spring 2004 was greater and applied nearer in time to the irrigation season than that applied for the 2003 season. Hence, we expected DOC availability to be greater in 2004 soils than in 2003, with the former producing greater runoff  $\text{DOC}_n$ . It is clear that other factors in addition to the magnitude and immediacy of manure applications were controlling net runoff DOC concentrations in manure treatments. The difference in DOC concentrations in irrigation inflows and runoff between years may be due to a difference in climate and its influence on DOC production in the soil (discussed later).

### The Relationship Between Runoff Sediment and Net Dissolved Organic Carbon Lost in Runoff

An increase in sediment concentration in the furrow stream increases the sediment mass and surface area exposed to water and should increase desorption and dissolution of soluble C. However, in 2003, the relationship between runoff  $\text{DOC}_n$  and runoff sediment concentrations was only generally evident (Fig. 3A and 1C) and was nearly lacking in 2004, except for the manure treatment in Irrigation 3 (Fig. 3B and 1D).

The reason for the general pattern of runoff  $\text{DOC}_n$  concentration we observed across the two seasons (Fig. 3A and 3B) may be a simple one. Regardless of treatment, 2003 soils either initially contained or produced considerably greater amounts of soluble organic C than in 2004 and, hence, the net runoff DOC concentration responded more directly to the quantity of eroded sediment that was carried in the stream flow. The greater available soluble organic C in 2003 soils likely stimulated microbial activity there, and the cyclic nature of this biologic activity may have caused the variation observed that season. As 2003 irrigations continued, the reserve of soil water soluble organic C amounts declined causing a decrease in runoff  $\text{DOC}_n$ .

In 2004, the production of soluble organic C in surface soils was reduced, and therefore sediment concentrations had less effect on runoff  $\text{DOC}_n$ . Since soluble organic C in the near-surface soil solution increases with air temperature during the growing season (Hope et al., 1994; Gregorich et al., 1998; Kalbitz et al., 2000), the consistently and substantially warmer air temperatures present in 2003 relative to 2004 likely contributed to greater DOC production in 2003. This contention is supported by annual observations from local irrigation water inflows, which indicate increasing DOC concentrations with increasing summer air temperatures (unpublished data, 2013). Note that the

seasonal changes in percolation water DOC did not follow that in runoff. This may have resulted because (i) percolation DOC concentration was driven primarily by percolation volume, and (ii) the soil source that supplied DOC to runoff water, i.e., the near surface soil, was different from that which supplied DOC to the percolation water (discussed later).

### Runoff Dissolved Inorganic Carbon Concentrations

The DIC in surface waters is comprised mainly of bicarbonate with small amounts of dissolved  $\text{CO}_2$  gas and an even smaller fraction of carbonate (Hope et al., 1994; Jarvie et al., 1997). Thus, the increase in  $\text{DIC}_n$  in the furrow stream during irrigation likely is derived from the dissolution of soil carbonate and bicarbonate salts. The similarity in the pattern of  $\text{DIC}_n$  and  $\text{DOC}_n$  runoff concentrations across irrigations and treatments (Fig. 3A–3D) suggests that runoff  $\text{DOC}_n$  concentrations also resulted from a simple dissolution process.

### Dissolved Organic Carbon and Dissolved Inorganic Carbon Transport Through Soil

The range in percolation DOC concentrations measured in the current study compare closely with values obtained from shallow groundwater (2.5 m) beneath manured fields of a dairy operation, 4.8 to  $55 \text{ mg L}^{-1}$  (Chomyca et al., 2008), but exceed those recorded at the 0.9-m depth under grassland soils, that is, 19 to  $28 \text{ mg L}^{-1}$  for a loamy sand and 3 to  $7 \text{ mg L}^{-1}$  for a silty clay loam (Don and Schulze, 2008).

Both percolation water DOC concentrations and mass losses increased with increasing percolation volume (Table 4), suggesting that bypass or macropore flow reduced the contact time between the percolating water and the soil. Therefore, the DOC percolating downward from the surface soil had less opportunity to adsorb to subsoils. This result supports the view that DOC export from these structured-soil profiles is largely controlled by the flow regime. When matrix flow dominates in these soils, or in nonstructured soils, DOC export becomes a function of the soil's DOC adsorption capacity and saturation (Jardine et al., 1989; Kalbitz et al., 2000; Don and Schulze, 2008) and microbial activity (Don and Schulze, 2008). The fact that percolation DIC concentration and mass losses also increased with percolation volume (Table 4) indicates that the DIC export through these profiles was also sensitive to flow regime and percolation water DIC–soil contact time. Soil pH typically increases with depth in these soils and, hence, carbonate solubility decreases with depth. This suggests that the main source of DIC in percolation water was from shallower soil depths and that the interaction of percolation water with subsoils caused DIC to precipitate.

### Carbon Balance

The irrigation water applied during the irrigation season input an overall average  $374 \text{ kg ha}^{-1}$  inorganic C and  $124 \text{ kg ha}^{-1}$  organic C to the corn field (Table 5). This inorganic C was about 10% of that measured for cropland irrigated with water from a karst watershed source (Schmitter et al., 2012). Our input or-

ganic C was four times greater than that reported by King et al. (2009) for a furrow-irrigated field under a Mediterranean climate and only 15% of that reported for a surface-irrigated crop under a subtropical, monsoonal climate (Schmitter et al., 2012).

The mean annual TOC losses from erosion and runoff in the current study, 531 kg ha<sup>-1</sup> OC (Fig. 6 and 7) were greater than the 30 to 320 kg ha<sup>-1</sup> range reported by Van Oost et al. (2007) from a survey of agricultural soils in the United States and Europe. The mean annual DOC leached from the current study's soils, 13.2 kg ha<sup>-1</sup> (Table 5), was 25 to 33% of the values reported for European croplands (Kindler et al., 2011). The discrepancy was mainly due to (i) the lesser percolation rate for the current study compared to Kindler et al. (2011) (caused by the large proportion of precipitation that occurred under low evapotranspiration demand in Europe), and (ii) the greater average installation depth of soil water percolation samplers used in the current study.

The net annual C-gain we measured in the manure treatment, 3.3 Mg C ha<sup>-1</sup> (Table 5), was slightly less than that measured for a manure-treated, no-till corn field harvested for grain (3.7 Mg C ha<sup>-1</sup>) (Shrestha et al., 2013). The similarity was largely fortuitous given that Shrestha et al. (2013) applied nearly three times more manure-C, removed 66% less biomass-C, and disregarded runoff and leaching C losses in their study in comparison to the current study. The negative annual C flux we observed for our non-manure amended treatments, -1.54 Mg C ha<sup>-1</sup> (Table 5), confirmed results reported for both non-manured, no till (Shrestha et al., 2013), and non-manured, tilled crops (Bono et al., 2008).

Manure applications across both years of the current study applied a total of 9.4 Mg C ha<sup>-1</sup> and produced a net gain in soil OC of 6.6 Mg C ha<sup>-1</sup> (3.3 Mg C ha<sup>-1</sup> net flux \* 2 yr). Assuming the added OC was incorporated into the 0- to 30-cm soil depth with an estimated mass of 4480 Mg ha<sup>-1</sup>, this would increase the soil OC concentration by 1.5 g C kg<sup>-1</sup> soil. This compares favorably with the 1.9 g C kg<sup>-1</sup> soil increase measured after 11.1 Mg C ha<sup>-1</sup> dairy manure was applied to the same soil, a Portneuf silt loam, nearby (Lentz, unpublished data, 2014). Manure increased stored soil C by direct addition and also indirectly. While treatments produced similar corn silage yields (Lentz and Lehrs, 2010), manure increased the residual biomass C produced by crops (relative to non-manure) via its influence on the residual/shoot biomass C ratio (Lentz, unpublished data, 2014).

Adding an average 4.7 Mg C ha<sup>-1</sup> as manure increased gaseous C emissions by 1.18 × each year in this low-OC soil cropped to silage corn. Under similar conditions Collins et al. (2011) reported little difference in C emissions from liquid manure-treated soils. By contrast, manure increased CO<sub>2</sub> emissions twofold when added to corn systems harvested for grain, which retained all corn stover residue in the field (Adviento-Borbe et al., 2010; Heller et al., 2010). The total seasonal DOC output via irrigation runoff was greater for manure than control treatments in 2004 (Table 5) due primarily to one significantly greater runoff DOC<sub>n</sub> event for manure vs. control furrows (Fig. 3B) and

greater runoff outflow rate for manure relative to control furrows, particularly in the third irrigation (Fig. 1B). In addition, the manure treatment more consistently raised net runoff DOC concentrations in 2004 compared with 2003 (Fig. 3B), which was likely related to the timing of the manure application. The manure was applied the previous fall for 2003 but in the spring for 2004.

Note that the mean DOC and DIC outputs in percolation waters were about twofold greater for control than for the manure (Table 5). While differences were not significant and, therefore, not conclusive, this trend is noteworthy because it is antithetical to the expectation that increasing soil organic content via manure additions increases both the DOC availability and the amount of DOC leached (Gregorich et al., 1998; Gallet et al., 2003). This result suggests that the direct effect of manure on soil DOC loss in percolation water may be mitigated by associated indirect effects. For example, manure can decrease pH (Liang et al., 2012) or increase salinity (Gallet et al., 2003), either of which may lead to reduced solubility and thus mobility of DOC in percolating water (Kalbitz et al., 2000; Hruska et al., 2009).

The standard errors of C-transfer mean values reported in Fig. 6 and 7 indicate the dispersion and uncertainty associated with the measurements. In most cases, the SE was 10% or less, but in the case of manure C input, soil C storage, PIC and POC in runoff, and DIC in percolation, SE exceeded 25%. Much of this variability may be attributed to year to year variations in inputs and their subsequent effects on C transfer. The SE for gaseous C emissions and soil biomass-C inputs were relatively small, about 10%; however, the actual uncertainty associated with these measurements could be greater owing to their dependence on emission and root/shoot distribution data that was derived from measurements made on the adjacent field.

## CONCLUSIONS

Few studies have documented the C balance in a cropped field. This research evaluated C inputs and outputs for a furrow irrigated corn field treated with either mineral fertilizer, dairy manure, or no amendment. The type of nutrient amendments applied to the irrigated corn harvested for silage substantially influenced the short-term C balance of the system. As expected, manure additions increased the short-term C storage in this productive agronomic soil. More surprising was the disproportionately small effect the added organic matter had on subsequent C exports, and the notable net C loss that occurred in the fertilized soil.

We anticipated manure-C additions would increase C losses from the soil (gas emissions, runoff, percolation) roughly in proportion to the C added (1.5× non-manured). However, the addition of organic-rich manure amendments increased soil C emissions from the soil by 1.18×, increased runoff DOC losses 1.04×, decreased particulate runoff TC 19%, and decreased percolate DOC 32%. Thus, the fraction of total C that remained in the manure-amended field at the end of each growing season was larger than anticipated due, in part, to the indirect effects of manure on soil characteristics and properties, such as aggregate stability.

Results of this study indicate that manure produces substantially less gaseous C emissions when applied to corn fields harvested for silage than for fields which retained stover residue. This observation suggests that manure applications may be used to minimize C emissions from corn crops.

The net dissolved C components exported in runoff, DOC<sub>n</sub> and DIC<sub>n</sub>, can be difficult to predict because they generally were not related to furrow outflow rate. Furthermore, runoff DOC<sub>n</sub> losses may be controlled, at least in part, by irrigation-inflow DOC concentrations, which differ temporally, presumably in response to biotic and environmental factors, perhaps external to the field. Predicting the amount of POC exported in runoff from fertilizer furrows likewise is not straight forward because the POC concentrations were not simply related to eroded sediment concentrations but appeared to be influenced by secondary effects of fertilizer on soils, which altered the fraction of POC contained in the eroded sediment.

Finally, because we observed similar concentration patterns for both DOC<sub>n</sub> and DIC<sub>n</sub> in furrow runoff, and because the relationships between percolate volume and percolate DOC and DIC concentrations were likewise similar, we conclude that the processes governing the transfer of soil C to the furrow and percolate streams are the same for both organic and inorganic forms. Further study is needed to determine the specifics of these processes.

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