Permanganate Oxidizable Carbon Reflects a Processed Soil Fraction that is Sensitive to Management

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Permanganate oxidizable C (POXC; i.e., active C) is a relatively new method that can quantify labile soil C rapidly and inexpensively. Despite limited reports of positive correlations with particulate organic C (POC), microbial biomass C (MBC), and other soil C fractions, little is known about what soil fractions POXC most closely reflects. We measured POXC across a wide range of soil types, ecosystems, and geographic areas (12 studies, 53 total sites, *n* = 1379) to: (i) determine the relationship between POXC and POC, MBC and soil organic C (SOC) fractions, and (ii) determine the relative sensitivity of POXC as a labile soil C metric across a range of environmental and management conditions. Permanganate oxidizable C was significantly related to POC, MBC, and SOC, and these relationships were strongest when data were analyzed by individual studies. Permanganate oxidizable C was more closely related to smaller-sized (53–250 μm) than larger POC fractions (250–2000 μm), and more closely related to heavier (>1.7 g cm^{-3}) than lighter POC fractions, indicating that it reflects a relatively processed pool of labile soil C. Compared with POC, MBC, or SOC, POXC demonstrated greater sensitivity to changes in management or environmental variation in 42% of the significant experimental factors examined across the 12 studies. Our analysis demonstrates the usefulness of POXC in quickly and inexpensively assessing changes in the labile soil C pool.

Abbreviations: C, soil carbon; fPOC, free particulate organic C; FSP, Farm System Project; HF, heavy fraction; KBS-LTER, Kellog Biological Station Long-Term Ecological Research; LF, light fraction; MBC, microbial biomass carbon; oPOC, occluded particulate organic C; POC, particulate organic C; POXC, permanganate oxidizable C; SIR, substrate induced respiration; SOC, soil organic C.

Particulate organic C and MBC are important C fractions that reflect key processes such as nutrient cycling and availability, soil aggregation, and soil C accrual (Wardle, 1992; Six et al., 1998; Wander, 2004). A large number of studies have shown that both POC and MBC are sensitive to changes in management such as reduced tillage, cover cropping and land use (Cambardella and Elliott, 1992; Wardle, 1992; Wander and Bidart, 2000; Grandy and Robertson, 2007). This sensitivity has led to wide adoption of these methods in soil science as indicators of change in the soil ecosystem (Wander, 2004; Gil-Sotres et al., 2005; Kaschuk et al., 2010).

As informative as POC and MBC are, they are expensive soil measures for most applications outside of a research setting. Although adaptations have been made to streamline the extraction process of POC (Marriott and Wander, 2006a) and MBC (Fierer et al., 2003), these methods remain costly due to the required labor and combustion analyzer to quantify the total C in the extracted fraction. In addition to the cost, there is a large degree of variation on how researchers extract

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and define POC and MBC fractions. For example, POC can be fractionated by size (Christensen, 2001) and/or by density (Six et al., 1998; Marriott and Wander 2006b). Microbial biomass C can be measured by a variety of methods including chloroform fumigation-extraction (Vance et al., 1987), direct extraction by chloroform (Fierer et al., 2003), chloroform fumigation-incubation (Jenkinson and Powlson, 1976) and substrate induced respiration (SIR; Anderson and Domsch, 1978). In addition, MBC is often adjusted with varying K_{ec} factors to adjust for extraction efficiencies of chloroform fumigation (Wardle, 1992; Joergensen, 1996). These methodological variations can make comparisons of POC and MBC across studies difficult, and even restrict drawing generalizations from a rich body of literature (Wander, 2004).

Potassium permanganate was first used to fractionate SOC via oxidation by Loginow et al. (1987). Lefroy et al. (1993), Blair et al. (1995), and others (Conteh et al., 1997; Shang and Tiessen, 1997; Bell et al., 1998), built on this work, using varying concentrations of permanganate (0.03–0.33 mol L^{-1} $KMnO_4$) to measure labile soil C. Studies that have used multiple concentrations of permanganate have consistently reported greater sensitivity to management with more dilute concentrations (0.02–0.033 mol L^{-1} $KMnO_4$) (Bell et al., 1998, Weil et al., 2003; Vieira et al., 2007).

Weil et al. (2003) further developed and streamlined this method, using 0.02 mol L^{-1} $KMnO_4$ to measure the 'active C' fraction of total SOC. This active C method, henceforth called 'permanganate oxidizable C (POXC), is rapid, inexpensive and can be modified for use in the field, and in low-cost fee-for-service soil testing for commercial growers (Idowu et al., 2008). Weil et al. (2003) showed that POXC was related to most measures of soil microbial activity, including MBC, SIR, soluble carbohydrate C, and total SOC. Other studies have found significantly positive relationships between POXC and microbial biomass (Melero et al., 2009a, 2009b; Culman et al., 2010, DuPont et al., 2010), phospholipid fatty acids (Jokela et al., 2009) and POC (Wuest et al., 2006; Mirksy et al., 2008).

Despite reports on positive correlations between POXC and other soil biologically mediated C fractions, there remains a lack of understanding regarding which fractions POXC most closely reflects. Moreover, little is known about how these relationships might change due to geographic, climatic, and/or edaphic factors. Finally, there is a lack of understanding regarding the sensitivity of POXC in reflecting changes in management relative to other SOC measures. We aimed to address all three of these knowledge gaps by examining the relationships between POXC and various soil C fractions (i.e., POC, MBC, and SOC) over a wide diversity of soil types, land uses and geographic areas across the USA. We hypothesized that POXC would be closely associated with the other measured soil C fractions and that POXC would be a sensitive and consistent indicator of changes due to management or environmental variation.

MATERIALS AND METHODS

Permanganate Oxidizable Carbon Nomenclature

Weil et al. (2003) originally called this method 'Active C', and since then others have called it various names including, 'chemically labile organic matter' (CLOM), 'readily oxidizable carbon' (ROC), labile carbon (LC) and 'permanganate oxidizable soil organic carbon' (POC; OxidC; PermOx C). While the name 'Active C' is intuitive for a lay audience, we feel that it lacks sufficient precision for the scientific community. Likewise, multiple names for the same method lead to ambiguity and a lack of standardization. Here, we propose that the scientific community adopt a unified and more exact name, 'permanganate oxidizable C' (POXC).

Description of Studies

Twelve studies were used in this comparative analysis for a total of 1379 samples from 53 sites (Table 1). These studies were selected to represent a wide range of soil types, ecosystems (intensively managed, extensively managed and natural) and geographic areas across the United States. Soils were sampled to different surface depths depending on the study, and several studies (Illinois, Kansas, Niles, Watkinsville) included soils from multiple depths (Table 2).

Particulate organic C and POXC were measured in all of the studies reported in this analysis, while MBC and SOC were only measured in a subset of studies. Microbial biomass C was measured in the Kansas, Niles, NY-Grain and Watkinsville studies; SOC was measured in all studies except Hunter and PA-Dairy. Soil texture was measured in Kansas, Niles, NY-Grain, NY-Veg, Watkinsville, and Winters studies. With the exception of POXC, all soil measurements (POC, MBC, SOC, texture) reported in this analysis were measured in the labs of the respective investigators (Table 1). All POXC measurements were performed at the W.K. Kellogg Biological Station (KBS), except for the Hunter and PA-Farms studies, which were measured by Mirsky et al. (2008) and the Farm System Project (FSP) study, measured by Spargo et al. (2011).

Permanganate Oxidizable Carbon

All POXC analyses were based on Weil et al. (2003). A detailed protocol of this method can be found at: http://lter.kbs.msu.edu/protocols/133 (verified 6 Jan. 2012). Briefly, 2.5 g of air-dried soil were weighed into polypropylene 50-mL screw-top centrifuge tubes. (Note: The method originally published by Weil et al. [2003] used 5.0 g of soil, but 2.5 g is now recommended [Weil, personal communication, 2011].) To each tube, 18 mL of deionized water and 2 mL of 0.2 *M* $KMnO_4$ stock solution were added and tubes were shaken for exactly 2 min at 240 oscillations per minute on an oscillating shaker. Tubes were removed from the shaker and allowed to settle for exactly 10 min. (Shaking times and settling times are very important with this method, so batches of 10 samples or less were run.) After 10 min, 0.5 mL of the supernatant were transferred into a second 50-mL centrifuge tube and mixed with 49.5 mL of deionized water. An aliquot (200 μL) of each sample was loaded into a 96-well plate contain-

Table 1. Characteristics of individual studies used in this analysis.

Study name	Location (geographic coordinates)	System/management	Number of sites (total *n*)	Reference(s)
Aurora	Aurora, NY (42°43′ N, 76°39′ W)	13 different cover crops planted in site previously in continuous corn	1 (30)	Maul, 2007
FSP	Farming Systems Project, Beltsville, MD (39°03′ N, 76°90′ W)	Long-term systems experiment; corn-soy-wheat rotations, cover crops	1 (20)	Spargo et al., 2011
Hunter	State College, PA (40° 43′ N, 77° 56′ W)	Long-term experiment with different crop rotation diversity and fertilizer sources	1 (141)	Mirsky et al., 2008
Illinois	DeKalb, Monmouth and Perry, Il (41°55′ N, 88°45′ W; 40°54′ N, 90°38′ W; 39°46′ N, 90°44′ W)	Corn-soy rotation with rye cover crop and different tillage regimes	3 (429)	M.M. Wander, unpublished data, 2011; Yoo et al., 2006
Kansas	Clay, Dickinson, McPherson, Ottawa and Saline Counties, KS (38°15′- 39°2′ N, 97°7′- 97°32′ W)	Native prairie vs. annual crop comparison	5 (60)	Beniston, 2009; Culman et al., 2010
KBS-LTER	Hickory Corners, MI (42°24′ N, 85°22′ W)	Long-term experiment; row crops, herbaceous and woody perennials	1 (56)	Grandy and Robertson, 2007
Niles	Niles, KS (38°58′ N, 97°28′ W)	Never-tilled annual crop conversion from tallgrass prairie	1 (36)	Beniston et al., 2009; DuPont et al., 2010
NY-Grain	Seneca and Yates Counties, NY (42°39′- 42°44′ N and 77°04′- 76°43′ W)	Grain farms over gradient of soil fertility	30 (118)	Schipanski et al., 2010; Schipanski and Drinkwater, 2011
NY-Veg	Columbia, Dutchess, Seneca, Tompkins, Ulster and Wayne Counties, NY; Lycoming County, PA (41°16′- 43°12′ N and 77°06′- 73°44′ W)	Organically managed vegetable farms with and without legume cover crops	15 (121)	L.E. Drinkwater , unpublished data, 2011
PA-Dairy	Centre, Lancaster, Union and Wyoming Counties, PA (40° 2′- 41°30′ N, 77°50′- 76° 02′ W)	Organically managed dairy farms	10 (118)	Mirsky , 2003
Watkinsville	Watkinsville, GA (33° 52′ N, 83° 25′ W)	Cropland and pasture under different management regimes and land-use histories	1 (112)	Franzluebbers et al., 2000; Franzluebbers and Stuedemann, 2002
Winters	Winters, CA (38° 36′ N, 121 °50′ W)	Irrigated row, vegetable and pasture crops under different tillage regimes	1 (144)	Lee et al., 2009

ing a set of internal standards, including a blank of deionized water, four standard stock solutions (0.00005, 0.0001, 0.00015, and 0.0002 mol L^{-1} $KMnO_4$), a soil standard and a solution standard (laboratory reference samples). All internal standards were analytically replicated on each plate. Sample absorbance was read with a SpectraMax M5 using Softmax Pro software (Molecular Devices, Sunnyvale, CA) at 550 nm. Permanganate oxidizable C was determined following Weil et al. (2003):

$$\text{POXC (mg kg}^{-1}\text{soil)}=\left[0.02\ \text{mol L}^{-1}-(a+b\times\text{Abs})\right]\times \left(9000\ \text{mg C mol}^{-1}\right)\left(0.02\ \text{L solution Wt}^{-1}\right)$$

where 0.02 mol L^{-1} is the concentration of the initial $KMnO_4$ solution, a is the intercept and b is the slope of the standard curve, Abs is the absorbance of the unknown soil sample, 9000 mg is the amount of C oxidized by 1 mol of MnO_4 changing from Mn^{7+} to Mn^{4+}, 0.02 L is the volume of $KMnO_4$ solution reacted, and Wt is the mass of soil (kg) used in the reaction.

Soil samples used to measure POXC always came from the same composite sample used to measure other C fractions. However, sometimes the soil processing differed due to sieving and/or grinding (Table 2).

Particulate, Microbial, and Total Soil Carbon Fractions

The POC methodologies in this comparative analysis varied considerably. Some studies in this analysis fractionated POC based on size (Kansas, KBS-LTER, Niles, Winters) and others fractionated POC based on density (Aurora, KBS-LTER, NY-Grain, NY-Veg). The KBS-LTER study fractionated POC based on both size and density (Table 2). Three of the four density-fractioned POC studies (Aurora, NY-Grain, NY-Veg) used the same method (Marriott and Wander 2006b). Briefly, free POC (fPOC) was separated from soil by floating on sodium polytungstate (1.7 g cm^{-3}). The remaining soil sample was shaken with sodium hexametaphosphate to disperse soil aggregates and then rinsed through a 53-μm filter. This step yielded occluded POC (oPOC). The LTER-KBS soil POC was fractionated by first floating inter-aggregate light fraction POC (LF-POC) on 1.7 g cm^{-3} sodium polytungstate. After shaking with sodium hexametaphosphate, intra-aggregate LF-POC was floated and collected as above. The heavy fraction (HF-POC) consisted of remaining mineral-associated aggregate C plus POC (Grandy and Robertson, 2007). For this analysis, inter- and intra-aggregate LF-POC were summed to yield total LF-POC. For comparative purposes, LF-POC was treated as conceptually similar

Table 2. Soil properties of individual studies used in this analysis.

Study name	Soil classification/description	Soil depth(s) sampled	POC class size(s)	Density fractionation? †	Soil size for POXC
			μm		μm
Aurora	Lima loam (Mesic Glossic Hapludalf)	0–15	>53	Yes, 1.70 g cm^{-3}	2000
FSP	Christiana (fine, kaolinitic, mesic Typic Paleudult), Matapeake (fine-silty, mixed, semiactive, mesic Typic Hapludult), Keyport (fine, mixed, semiactive, mesic Aquic Hapludult), and Mattapex (fine-silty, mixed, active, mesic Aquic Hapludult) silt loams	0–20	2000–53	No	2000
Hunter	Hagerstown series (fine, mixed, mesic, Typic Hapludalf)	0–15	2000–53	No	2000
Illinois	Herrick silt loam (fine, montmorillonitic, mesic Aquic Argiuoll), Muscatine silt loam (fine-silty mixed mesic Aquic Argiuoll) and Drummer silty clay loam (fine, silty mixed mesic Typic Haplaquoll)	0–10; 10–20; 20–30	2000–53	No	Ground
Kansas	Geary (fine-silty, mixed, superactive, mesic Udic Argiustoll); Hobbs (fine-silty mesic Mollic Ustifluvent); Goessel (silty-clay mesic Typic Haplustert); Detroit (fine mesic Pachic Argiustoll); Muir (fine-silty mesic Cumulic Haplustoll)	0–10; 10–20; 20–40; 40–60; 60–80; 80–100	2000–250; 250–53	No	500
KBS-LTER	Kalamazoo (fine-loamy, mixed, mesic Typic Hapludalf) and Oshtemo (coarse-loamy, mixed, mesic Typic Hapludalf) series	0–5	8000–2000; 2000–250; 250–53	Yes, 1.60 g cm^{-3}	Ground
Niles	Geary silt loam (fine-silty, mixed, superactive, mesic Udic Argiustoll)	0–10; 10–20; 20–40; 40–60; 60–80; 80–100	2000–250; 250–53	No	500
NY-Grain	Sandy clay loams, silt loams, clay loams; mixed, active Hapludalf	0–20	>53	Yes, 1.70 g cm^{-3}	2000
NY-Veg	Sandy, silty and gravely loams; mixed, active/semiactive, Hapudalfs, Dystrudepts, Fluvaquents and Upidpsamments	0–20	>53	Yes, 1.70 g cm^{-3}	Not sieved
PA-Dairy	Various mesic Typic Fragiaquult, Typic Dystrochrept, Typic Hapludult, and Typic Hapludalf; Various mesic Aeric Fragiaquept, Lithic Hapludalf, Typic Fragiochrept, and Lithic Dystrochrept	0–15	2000–53	No	2000
Watkinsville	Cecil– Madison–Pacolet (fine, kaolinitic, thermic Typic Kanhapludult) soil series with sandy loam, loam, or sandy clay loam surface textures	0–5; 5–12.5	4750– 60	No	Ground
Winters	Myers clay (fine, montmorillonitic, thermic Entic Chromoxerert), Hillgate loam (fine, montmorillonitic, thermic Typic Palexeralf), and San Ysidro loam (fine, montmorillonitic, thermic Typic Palexeralf)	0–15	2000–1000; 1000–250; 250–53	No	Ground

† Density fractionation made with sodium polytungstate. Final density used is reported for each study. POXC = permanganate oxidizable carbon; POC = particulate organic carbon

to fPOC, and oPOC was treated as similar to HF-POC. Size classes of POC also varied, but most fell within the range of 53 to 2000 μm (Table 2).

Soil MBC was performed with chloroform fumigation-incubation (Jenkinson and Powlson, 1976; Watkinsville study), chloroform fumigation-extraction (Vance et al., 1987; Niles and Kansas studies) or chloroform direct extraction method (Fierer et al., 2003; NY-Grain study). Total SOC was determined with a direct combustion analyzer. See individual studies for more details of measurements taken (Table 1).

Statistical Analyses

Linear relationships between POXC and POC, MBC and SOC were tested with the *lm*() function in R (R Core Development Team, 2011). The effects of covariates were tested by adding model variables into the linear regression using *lm*(). The sensitivity of POXC, POC, MBC, and SOC in regards to experimental factors (land use, tillage, sites, soil depth, etc.) were tested with analysis of variance models using the function *aov*(). For each study, all respective experimental factors were included in the model and four separate analyses were run, using POXC, POC, MBC, or SOC as a response variable. F-statistics from model output were used to assess the relative magnitude of the effect of that factor on the C fraction, that is, how sensitive that soil C fraction was to experimental factors. Bivariate relationships and least squared regression lines between the soil C fractions were graphed with the package *ggplot2* in R.

RESULTS AND DISCUSSION

Summary Statistics and Aggregated Data

There were large differences in relative sizes of each soil C fraction with means of POC averaging roughly four or more times the size of POXC and MBC (Table 3). Over all the studies, POC comprised roughly 14% of the total organic carbon in the soil. In contrast, POXC and MBC made up only 4 and 2% of the total SOC, respectively. All fractions except POXC were highly right skewed, and as a result, all data except POXC were log transformed before analyses (Table 3).

Permanganate oxidizable C was significantly related to all measured soil C fractions when data were aggregated over all 12 studies (Fig. 1). POC, MBC, and SOC explained 0.26, 0.44, and 0.58 of the variation in POXC, respectively. When relationships of POXC and other soil C fractions were analyzed by individual study, relationships greatly improved. In all studies, POXC was significantly related to POC (Fig. 2, Table 4). Coefficients of determination ranged from 0.14 to 0.79 (Table 4). In general, the studies with only one site (Table 1) demonstrated better relationships between POXC and POC, indicating that edaphic and environmental factors from multiple sites contributed to unexplained variation in the data.

Permanganate Oxidizable Carbon and Size-Fractionated Particulate Organic Carbon

In all studies that fractionated POC by size, POXC was more closely related to smaller sized POC fractions than larger fractions (Table 4). In the Winters study, POC was fractionated into three size classes and the largest two fractions were pooled together in Table 4. Closer examination of all three fractions in this study reveals that POXC explained 4, 31, and 63% of the variation in C concentration of the 1000- to 2000-, 250- to 1000-, and 53- to 250-μm fractions, respectively (Fig. 3). Compared with larger POC fractions, the 53- to 250-μm fraction tends to have a smaller C/N ratio, a larger proportion of microbial biomass, and a longer turnover time (von Lutzow et al., 2007). Since smaller-sized POC is typically organic material that has been more decomposed than larger-sized POC (Six et al., 1998; Wander 2004), these relationships suggest that POXC reflects a more processed, degraded fraction of soil C.

Permanganate Oxidizable Carbon and Density-Fractionated Particulate Organic Carbon

Permanganate oxidizable C was more closely related to the occluded (heavy) fraction of POC than the free (light) fraction of POC in every density fractionated study (Table 4; Fig. 4). The low strength of relationship between POXC and POC in the Aurora study may have resulted from the short duration of time since the treatments were imposed. Soils were analyzed after the first year of growing a variety of different cover crops following 53 yr in continuous corn. Treatment differences were small compared with other studies evaluated in this comparative analysis. Free POC consists of recent residues from roots and shoots and occluded POC consists of more decomposed litter inputs physically protected from further degradation within soil aggregates (Wander, 2004). Overall, our results were consistent with POXC being an early indicator of C change in soils, and more closely related to more decomposed POC pools.

Table 3. Summary statistics of each soil fraction by individual study†.

Study	POXC ($mg\ C\ kg^{-1}$ soil) Min, Median, Max	Mean		SD	POC ($mg\ C\ kg^{-1}$ soil) Min, Median, Max	Mean		SD	MBC ($mg\ C\ kg^{-1}$ soil) Min, Median, Max	Mean		SD	SOC ($g\ C\ kg^{-1}$ soil) Min, Median, Max	Mean		SD
Aurora	576, 666, 801	668	±	54	1442, 3257, 4921	3275	±	865					11, 19, 25	19	±	3
FSP	376, 447, 567	443	±	43	2533, 3134, 4933	3237	±	533					13, 15, 20	16	±	2
Hunter	416, 528, 660	536	±	48	1220, 2970, 5860	3135	±	839								
Illinois	69, 638, 1297	676	±	263	228, 1044, 7539	1610	±	1307					6, 21, 64	23	±	10
Kansas	81, 326, 1086	378	±	242	110, 510, 5870	1175	±	1418	10, 55, 386	94	±	94	3, 10, 31	12	±	6
KBS-LTER	370, 730, 1305	784	±	230	776, 1778, 5540	2102	±	1123					8, 16, 55	20	±	11
Niles	124, 359, 1160	465	±	331	120, 670, 7350	1618	±	2061	37, 116, 386	151	±	110	5, 14, 33	16	±	9
NY-Grain	356, 640, 955	631	±	126	793, 2087, 4091	2128	±	671	9, 103, 394	130	±	88	11, 17, 34	18	±	5
NY-Veg	154, 600, 983	601	±	193	1150, 3220, 20730	4512	±	3984					7, 22, 54	24	±	9
PA-Dairy	369, 548, 699	552	±	67	1331, 3885, 7077	3848	±	1130								
Watkinsville	201, 720, 1468	814	±	411	958, 3620, 20780	6775	±	5834	220, 551, 1490	645	±	333	5, 15, 49	19	±	12
Winters	294, 599, 857	597	±	102	1034, 1864, 3638	1907	±	531					6, 10, 13	10	±	1
Totals	69, 588, 1468	626	±	242	110, 2148, 20780	2755	±	2734	9, 208, 1490	319	±	331	3, 17, 64	19	±	10

† Min = Minimum; Max = Maximum; SD = Standard deviation

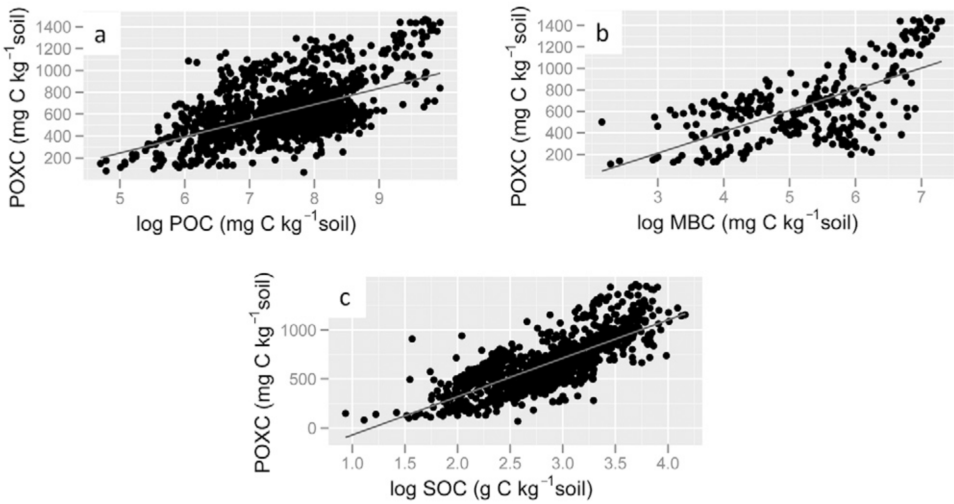

Fig. 1. Relationship between permanganate oxidizable C (POXC) and soil C fractions [(a) particulate organic carbon (POC), (b) microbial biomass carbon (MBC), and (c) soil organic carbon (SOC)]. Coefficients of determination (r^2) between POXC and POC (n = 1359), MBC (n = 326), and SOC (n = 1115) were 0.26, 0.44 and 0.58, respectively.

Permanganate Oxidizable Carbon and Microbial Biomass Carbon

Permanganate oxidizable C was significantly related to MBC, although the strength of the relationship varied with each study (Table 4). For example, the Niles study had the strongest relationship (r^2 = 0.97) and the NY-Grain study had the lowest (r^2 = 0.11). The weak relationship in the NY-Grain study was mostly attributable to differences in variability among multiple fields. If these fields (sites) were included in the linear model, the coefficient of determination increased dramatically to 0.89. Since both MBC and POXC are based on chemical extractions of labile soil C, the agreement between these two methods is logical. Weil et al. (2003) found high positive correlation (r^2 = 0.72) between MBC and POXC across mid-Atlantic farms. Subsequent studies have shown positive correlations between POXC and MBC (Melero et al., 2009a, 2009b; Culman et al., 2010), although a weak relationship has been reported in anaerobic paddy rice soils (Tirol-Padre and Ladha, 2004) and in a clay loam in Spain (Melero et al., 2011).

Permanganate Oxidizable Carbon and Soil Organic Carbon

Soil organic C and POXC were significantly related in every study, except the Aurora study (Table 4, Fig. 5). The relationship between POXC and SOC was generally stronger than POXC with other soil C fractions in nearly every study. A strong positive relationship between POXC and SOC has been reported previously (Weil et al., 2003; Tirol-Padre and Ladha, 2004; Wuest et al., 2006; Jokela et al., 2009). The relationship may be stronger due to similar methodologies of POXC and SOC, as SOC relies on complete oxidation of all soil C, while POXC relies on partial oxidation of the C pool.

Edaphic Covariates of Permanganate Oxidizable Carbon

Major edaphic covariates of POXC were examined in a subset of studies to determine if these covariates could account for some unexplained variation between POXC and other soil C fractions.

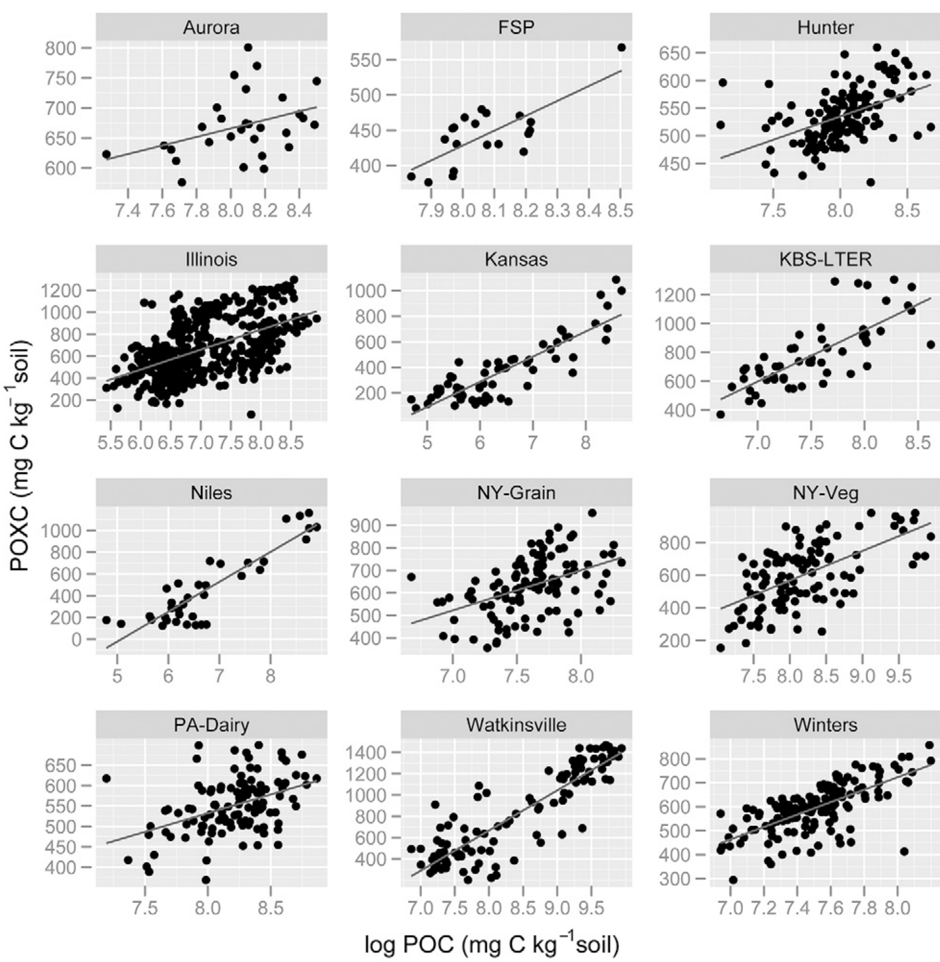

Fig. 2. Relationship of permanganate oxidizable C (POXC) and particulate organic C (POC) for individual studies. Coefficients of determination are reported in Table 4.

Table 4. Coefficients of determination (r^2) between permanganate oxidizable C (POXC) and particulate organic C (POC), microbial biomass C (MBC) and soil organic C (SOC) of individual studies‡.

Study	Total POC		Density-defined POC¶ fPOC/LF		Density-defined POC¶ oPOC/HF		Size-defined POC 250–2000 µm		Size-defined POC 53–250 µm		MBC		SOC	
Aurora	0.14	†	0.07		0.08								0.01	
FSP	0.57	**											0.77	***
Hunter	0.26	***												
Illinois	0.28	***											0.79	***
Kansas	0.68	***					0.45	***	0.74	***	0.73	***	0.85	***
KBS-LTER	0.58	***	0.58	***	0.76	***	0.08	*	0.35	***			0.76	***
Niles	0.66	***					0.47	***	0.72	***	0.97	***	0.95	***
NY-Grain	0.19	***	0.00		0.23	***					0.11	***	0.71	***
NY-Veg	0.36	***	0.03	*	0.51	***							0.60	***
PA-Dairy	0.18	***												
Watkinsville	0.79	***									0.69	***	0.83	***
Winters	0.47	***					0.25	***	0.63	***			0.71	***

* Significant at $P < 0.05$.

** Significant at $P < 0.01$.

*** Significant at $P < 0.001$.

† Significant $P < 0.10$.

‡ POC fractions include total POC, density-defined (free POC [fPOC] or light fraction [LF]; occluded POC [oPOC] or heavy fraction [HF]), and size-defined (2000–250 µm; 250–53 µm).

¶ Density-defined POC fractions differed by methods; fPOC and LF fractions were floated with sodium polytungstate while oPOC and HF were not. See methods for more details.

Covariates were added into the linear model and compared against model output without the covariates (Table 5). Overall, soil texture (clay and sand) contributed little to improving relationships between POXC and POC, MBC, or SOC. Texture varied greatly across the six studies that measured this property, with respective minimum, mean and maximum values of 38, 406, and 873 g kg^{-1} for sand and 79, 234, and 584 g kg^{-1} for clay. Although SOC is often positively correlated with the percentage of clay (Nichols, 1984; Schimel et al., 1994; Six et al., 2002) clay content did not improve relationships in this analysis.

Adding total SOC or depth of the soil sample into the model generally improved relationships of POXC and the other C fractions (Table 5). Most notably, the relationship between POXC and MBC was greatly improved, when adjusted for SOC and soil depth. This result is likely a reflection of the nonlinear nature between POXC and MBC under conditions where recalcitrant organic matter and its placement in the soil profile interact.

Sensitivity of Permanganate Oxidizable Carbon in Detecting Changes Management/ Experimental Factors

Labile soil C fractions, such as POC and MBC, are important indicators of changes in soil ecosystems brought about by management practices. Here we considered if POXC can serve as an indicator of changes in management or other experimental factors, in a similar manner as POC and MBC. Four separate analysis of variance (ANOVA) models were run on each study with POXC, POC, MBC, or SOC as the response variable against all experimental factors (e.g., management regimes, different fields, multiple depths, etc.) of a particular study.

Permanganate oxidizable C, POC, MBC, and SOC were largely consistent regarding which experimental factors in a study were statistically significant (Table 6). (Only those experimental factors which were found significant ($\alpha = 0.10$) in one or more of the C fractions were included in Table 6.) The total number of experimental factors where a soil C fraction was found significant and POXC was not significant was five factors

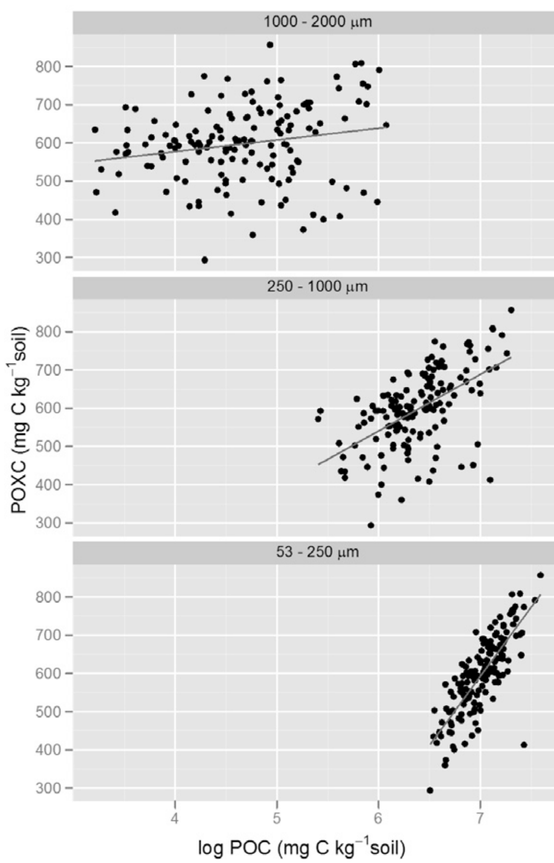

Fig. 3. Relationship of permanganate oxidizable C (POXC) and three particulate organic C (POC) sizes in the Winters study. Coefficients of determination are 0.04, 0.31, and 0.63 for the largest, medium and smallest size class, respectively.

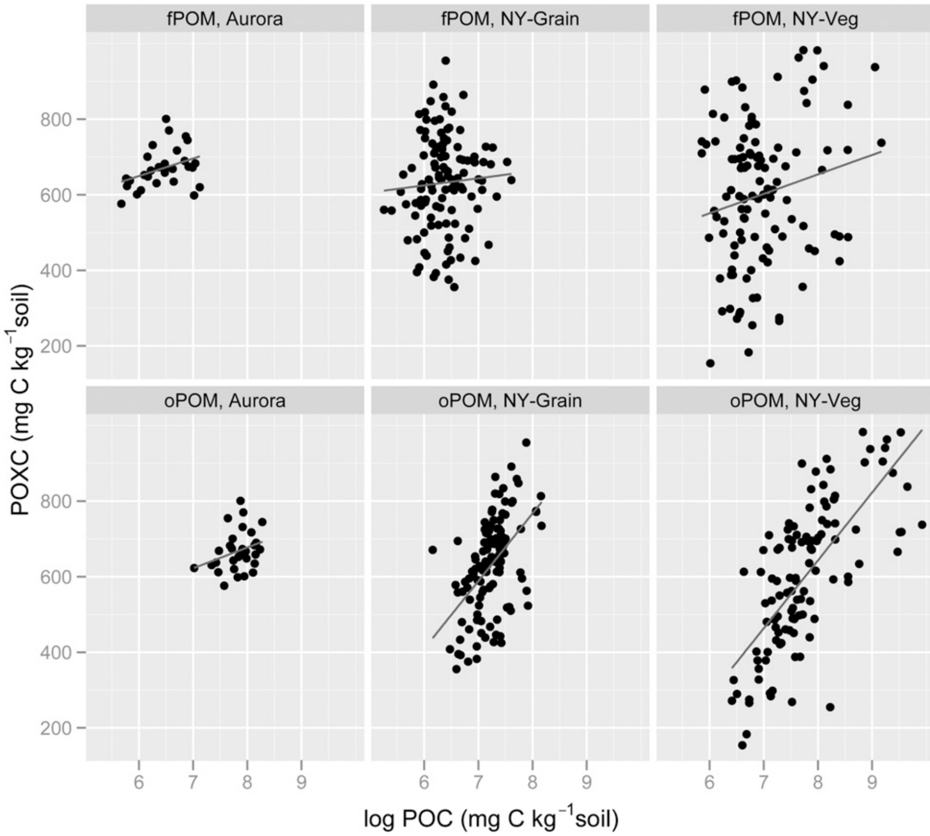

Fig. 4. Relationship of permanganate oxidizable C (POXC) and free POC (fPOC), and occluded POC (oPOC) in the Aurora, NY-Grain and NY-Veg studies. Coefficients of determination are reported in Table 4.

for POC, two factors for MBC, and one factor for SOC. The total number of experimental factors where POXC was found significant and another soil C fraction was not significant was one factor for POC, two factors for MBC, and one factor for SOC (Table 6).

F-statistics generated from the ANOVA models represent the magnitude of the effect for each C fraction. In other words, we define the sensitivity of each C fraction as the F-statistic, where greater sensitivity of a fraction relative to other fractions is reflected by a larger F-statistic. Permanganate oxidizable C

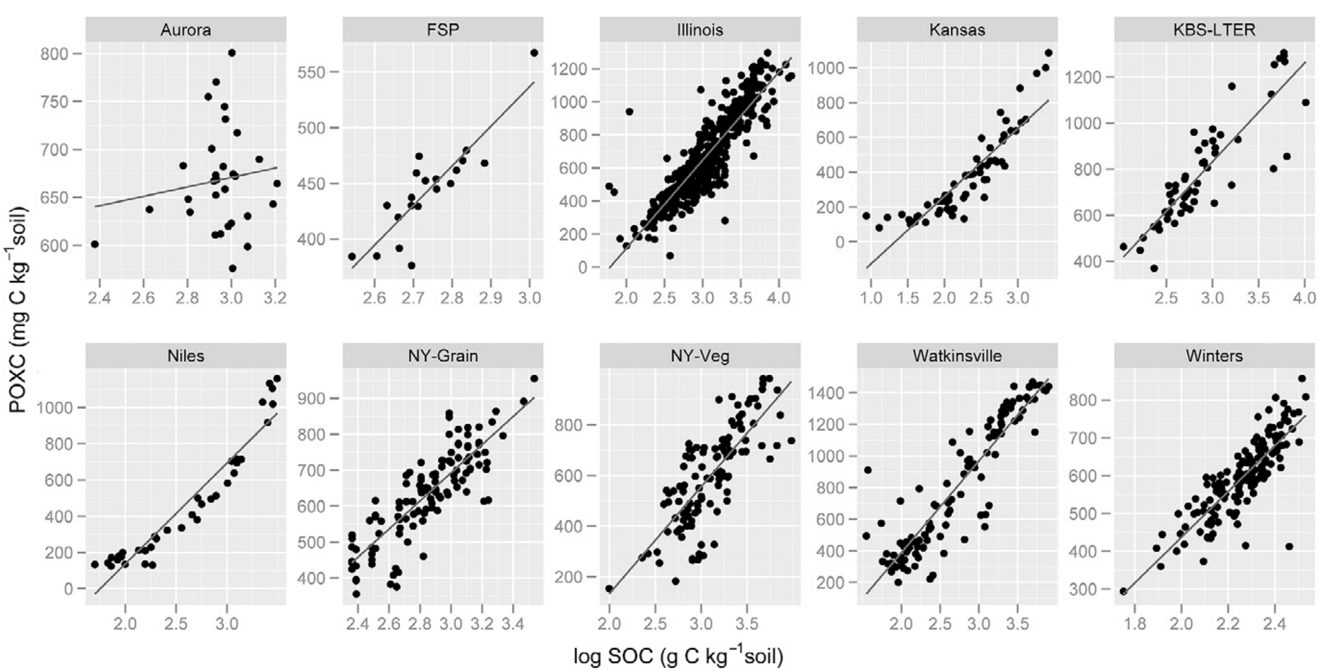

Fig. 5. Relationship of permanganate oxidizable C (POXC) and soil organic C (SOC) by individual studies. Coefficients of determination are reported in Table 4.

had larger a F-statistic than the other three fractions in 13 out of the 31 comparisons (42% of the time), while POC had the largest F-statistic in 10 out of the 21 comparisons (32%). Microbial biomass C and SOC were only measured on a subset of studies, and MBC had the largest F-statistic 1 out of 11 comparisons (9%), while SOC had the largest F-statistic in 7 out of 24 comparisons (29%). These findings indicate that POXC is a sensitive indictor to experimental factors typically examined in soil science field experiments.

Permanganate oxidizable C was a more sensitive indicator of differences in management than the other measured fractions in the Hunter (Fertilizer, Rotation) and Watkinsville (Land Use)

Table 5. Coefficients of determination (r^2) between POXC and other soil C fractions (POC, MBC, and SOC) with and without edaphic covariates†.

Soil C fraction	POXC only (no covariate)	POXC +			
		Clay	Sand	SOC	Depth
POC (n = 583)	0.63	0.66	0.67	0.67	0.74
MBC (n = 326)	0.44	0.47	0.44	0.86	0.79
SOC (n = 583)	0.52	0.56	0.53	–	0.82

† The six studies with texture data (Kansas, Niles, NY-Grain, NY-Veg, Watkinsville and Winters) were included in the POC and SOC analyses; analyses with MBC were performed on the four studies with MBC data (Kansas, Niles, NY-Grain and Watkinsville). POXC, permanganate oxidizable C; POC, particulate organic C; MBC = microbial biomass C; SOC = soil organic C.

Table 6. Comparison of the sensitivity of permanganate oxidizable C (POXC), particulate organic C (POC), microbial biomass C (MBC) and soil organic C (SOC) in detecting factors related to experimental design of each study. F-statistics were generated from ANOVA models from each study with either POXC, POC, MBC, or SOC as the response variable. Only the F-statistics of statistically significant factors (both main effects and interactions) are shown. Bolded F-statistics indicate the method that demonstrated comparatively greater sensitivity†.

Study	Experimental factor	F-statistic							
		POXC		POC		MBC		SOC	
Aurora	Cover crop	1.6		**6.3**	***			0.9	
FSP	Cropping system	1.3		**2.8**	.			0.4	
Hunter	Year	**10.2**	***	9.2	***				
	Fertilizer	**49.5**	***	15.6	***				
	Rotation	**18.2**	***	15.6	***				
	Fertilizer/rotation	**4.4**	***	2.5	*				
Illinois	Site	**427.9**	***	3.0	.			369.4	***
	Depth	151.2	***	**365.9**	***			59.7	***
	Tillage	1.0		1.5				**2.6**	.
	Site/depth	2.5	*	**2.9**	*			2.6	*
	Site/tillage	2.5	*	1.8	.			**2.7**	*
	Site/tillage/cover crop	**5.7**	***	1.3				3.2	**
Kansas	Land use	17.6	***	32.6	***	**94.4**	***	28.9	***
	Depth	**61.4**	***	36.2	***	29.7	***	35.3	***
	Site	2.3	*	2.9	*	1.5		**6.5**	***
	Land use/depth	1.8		**2.9**	*	2.8	*	1.7	
KBS-LTER	Cropping system	18.5	***	17.2	***			**49.8**	***
Niles	Land use	0.0		**12.9**	**	10.6	**	0.1	
	Depth	**484.6**	***	80.0	***	214.6	***	138.3	***
	Land use/depth	0.2		**2.6**	.	0.1		0.2	
NY-Grain	Field	23.5	***	13.3	***	13.2	***	**76.1**	***
NY-Veg	Field	24.0	***	17.5	***			**29.5**	***
PA-Dairy	Farm	**21.3**	***	21.0	***				
	Fields	**10.9**	***	5.2	***				
	Farm/fields	**5.7**	**	0.9					
Watkinsville	Land use	**25.4**	***	13.0	***	6.9	***	17.4	***
	Depth	1388.7	***	**1647.8**	***	527.2	***	1287.6	***
	Land use/depth	**8.7**	***	6.9	***	1.9	*	4.2	***
Winters	Date	8.5	**	**18.8**	***			1.8	
	Tillage	3.3	†	8.1	**			**14.0**	***
	Date/tillage	11.2	**	**31.6**	***			15.8	***
Total instances F-statistic was greatest		13		10		1		7	
Total number of comparisons		31		31		11		24	
Percentage when method was the most sensitive		**0.42**		**0.32**		**0.09**		**0.29**	

* Significant at $P < 0.05$.

** Significant at $P < 0.01$.

*** Significant at $P < 0.001$.

† Significant at $P < 0.10$.

studies. Permanganate oxidizable C was intermediate in sensitivity to management differences, as compared with POC, MBC, and SOC in the Aurora (Cover Crop),Farming Systems Project (FSP; Cropping System) and Kellog Biology Station Long-Term Experimental Research (KBS-LTER; Cropping System) studies. Permanganate oxidizable C was less sensitive to management than the other measures in the Kansas (Land Use), Niles (Land Use), and Winters (Tillage) studies (Table 6). Three of these studies involved the initiation of a manipulated management treatment (Aurora—different cover crops following long-term continuous corn, Niles—no-till conversion of native grassland, Winters—tillage after period of no till). In these studies, POC had one of the largest F-statistics, suggesting that POC may be well suited for detecting the earliest changes of a soil ecosystem in flux. However, our findings are consistent with a number of studies that have demonstrated the ability of POXC in detecting changes in management involving tillage and inputs after 2 to 4 yr (Quincke et al., 2007; Melero et al., 2009b; DuPont et al., 2010; Lewis et al., 2011; Lopez-Garrido et al., 2011).

Overall, POXC was more sensitive than POC and MBC in detecting site differences (Illinois, NY-Grain, NY-Veg, PA-Dairy). However, the sensitivity of POC, MBC, and POXC was not distinguishable regarding the effects of depth (Illinois, Kansas, Niles, Watkinsville) and time of sampling (Hunter, Winters; Table 6). Permanganate oxidizable C may have an advantage for detecting site differences (such as due to soil type, pH, climatic variations, etc.), but may not have a clear advantage over other soil C fractions for detecting differences due to depth or temporal dynamics.

CONCLUSIONS

Permanganate oxidizable C was significantly related to all soil C fractions examined in this analysis, including POC, MBC, and SOC. Permanganate oxidizable C was more strongly related to heavier and smaller POC fractions than lighter and larger POC fractions, indicating that it reflects a more processed, stabilized pool of labile soil C. This suggests that POXC may be well suited to track management practices that promote soil C sequestration, making it a particularly useful indicator for soil quality research. Permanganate oxidizable C appears to be equally capable as POC, MBC, and SOC in detecting differences in soils due to management or environmental factors. There were no trends of nonlinear relationships across textural or geographic gradients, suggesting that POXC would be useful for soil studies throughout the United States. The sensitivity of this method and the relative ease of measurement suggest that POXC can be used to routinely evaluate biologically active soil C.

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