Biogeochemistry of terrestrial soils as influenced by short-term flooding

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Abstract Many terrestrial soils in the US Midwest are temporally flooded during the spring. The effects of short-term flooding on biogeochemical processes that occur in these soils are not fully understood and are the subject of this study. To evaluate these processes we investigated the redox-induced changes in the soil solution for three-cultivated and three-uncultivated/ forest soils with different organic matter concentrations. The soils were flooded for 1, 3, 7, and 14-days under anoxic conditions in a biogeochemical reactor. Samples were analyzed for Eh; pH; NO_3^-; NH_4^+; total dissolved Mn and Fe; soluble P; dissolved organic and inorganic carbon (DOC–DIC); and evolved CO_2. We found strongly contrasting responses of the terrestrial soils to flooding. Reducing conditions were established quickly in the uncultivated and more slowly in the cultivated soils. Concomitant changes in pH were higher for the uncultivated soils. The uncultivated soils showed a higher increase in the amount of NH_4^+, P, Fe, Mn than the cultivated soils over the 14-day incubation. The total amount of carbon decomposed was much greater for the uncultivated soils with approximately 900 µg C (CO_2 + DOC + DIC) decomposed per gram of soil compared to a total decomposition of 240 µg C g_{soil}^{-1} for the cultivated soils indicating differences in the type of carbon decomposed. The rapid onset of reducing conditions for the uncultivated soils is attributed to a reactive carbon component that is either absent or occluded in the cultivated soils. This study demonstrates that the biogeochemically-induced changes in carbon dynamics in terrestrial soils are strongly influenced by short-term flooding and the history of soil management.

Keywords Biogeochemistry · Carbon cycling · Flooding · Redox · Terrestrial soils

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Abbreviations

ACRE	Purdue University Research Farm
Ar	Argon
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DRP	Dissolved reactive phosphorus
Eh	Redox potential
ICP-OES	Inductively coupled plasma with optical emission

Redox   Reduction–oxidation
TOC   Total organic carbon

Introduction

Many terrestrial soils have aquic features and are saturated for periods of weeks to months each year. In the US Midwest, for instance, about 20% of the terrestrial soils have aquic features and are classified as Aquolls and Aqualfs according to the US Soil Taxonomy and Classification System. In addition to the historical aquic soil conditions, nowadays many well drained terrestrial soils may experience temporally flooding as a consequence of increasing moisture extremes due to climate changes (Lins and Slack 1999). Flooding of terrestrial soils may induce biogeochemical changes in those soils, such as changes in the carbon and nutrients cycling, and that can lead to great environmental and agriculture concerns. For instance, Fiedler and Kalbitz (2003) found that dissolved organic carbon (DOC) production increased in flooded forest soils and soluble DOC might reach underground water thus increasing the risk of groundwater contamination. Phosphorus can dissolve upon flooding of terrestrial soils (Hutchison and Hesterberg 2004). Elevated soluble P concentrations in surface waters have caused problems, such as algal blooms and eutrophication in streams and lakes.

Terrestrial soils under flooding and reducing conditions may behave like wetland soils that are often saturated for a more prolonged period of time during the year. Wetland soils have been extensively studied and it is known that many redox (reduction–oxidation) sensitive chemical species that are stable under aerobic (oxidizing) conditions, such as NO_3^-, Fe, and Mn, often undergo reduction and can be released from the soil to the solution phase during periods of flooding (e.g., Ponnamperuma 1972; Reddy and Patrick 1976; Kirk et al. 2003). Typically, large amounts of organic carbon accumulate in wetland soils, and carbon mineralization drives important redox reactions and subsequent chemical transformations in these soils (e.g., Bridgham et al. 1998; Yao et al. 1999).

In contrast to wetland soils, knowledge about the biogeochemical changes that occur under periodic flooding and anoxic conditions for terrestrial soils and the effects of these changes on soil properties is limited. Previous studies (Peters and Conrad 1996; Scalenghe et al. 2002; Hutchison and Hesterberg 2004; De-Campos et al. 2009) showed that reducing conditions were established immediately after anoxic incubation of terrestrial soils. They observed sequential reduction processes similar to those reported for wetland soils, i.e., reduction of NO_3^- followed by reduction of Mn, SO_4, and Fe. Hutchison and Hesterberg (2004) found that the onset of redox reactions in a non-dextrose amended terrestrial soil was much slower than in a dextrose amended soil under flooding. This finding indicates that the amount of readily available carbon in terrestrial soils under flooding can influence redox reactions. Hutchison and Hesterberg (2004) also found a strong correlation between the dissolution of phosphorus and DOC upon the onset of reducing conditions and the CO_2 production indicated the potential for microbially mediated reduction reactions toward the changes in the solution chemistry.

In a companion paper, we examined the influence of short-term flooding on aggregate stability of the same suite of soils studied here (De-Campos et al. 2009). The focus of the earlier publication was on aggregate stability and we found that the aggregate stability of terrestrial soils is highly affected by changes in their biogeochemistry upon flooding. Overall, the results showed that strongly reducing conditions followed by increases in the solution concentrations of redox-sensitive metals (Mn and Fe), alkaline metals (Ca, Mg, and K), and DOC are well correlated with decreasing soil aggregate stability. These previous findings stress the needs to investigate biogeochemical processes that occur in terrestrial soils upon flooding to better understand their effects on soil properties.

As reported for wetland soils, the rates of redox reactions and associated biogeochemical transformations in terrestrial soils upon flooding depend on the presence of organic carbon. Larger amounts of readily available carbon sources, such as added dextrose, may enhance redox reactions and nutrient cycling (Hutchison and Hesterberg 2004). Terrestrial soils have a wide range of organic matter content and that may exhibit different degrees of redox reactions and biogeochemical processes under reducing conditions. Furthermore, soil management can impact the source of carbon in soil organic matter (Schnitzer and Khan 1989). Forest soils with more readily available source

of carbon, such as fulvic acids, should induce faster redox reactions upon flooding than agriculture soils.

Soil organic matter and management practices can play important roles in redox reactions in terrestrial soils. However, it is not clear to what extent the short-term reducing conditions and biogeochemical changes in these soils are affected by the amount and type of soil organic matter or by the history of soil management. In this study, we systematically investigated the influence of short-term water saturation on terrestrial soils of varying organic matter concentrations and management history using a biogeochemical reactor. We hypothesized that flooding induced redox reactions and chemical release in terrestrial soils will increase with the amount of soil organic matter and that cultivation decreases redox reactions and nutrient cycling.

Materials and methods

Soils collection and characterization

The surface horizons (0–10 cm depth) of three cultivated and three uncultivated/forest soils were sampled from the Purdue University Research Farm (ACRE) and studied in the laboratory. The sampled areas were chosen from the criteria that these soils were close enough to have the same climate, landscape position, drainage, settlement history, management history, and represented continuous soil series on the soil map; to avoid any uncertainty in comparisons between cultivated and uncultivated soils. Cultivated soils are soils that have been used for crop production (mainly corn-soy bean rotation) for the last 20 years. Uncultivated soils are soils under forest that have not been disturbed by any agricultural activity at least in the past 20 years, according to the Purdue farm records. The unculti-vated soils are under the same type of vegetation cover and conservation history. They are located in forest patches of about 1 km^2 in size that are surrounded by agriculture areas. The density of trees in the patches is similar and some trees, such as oaks, are tall enough to indicate that the forest patches have not been disturbed for some time. These forest patches can be remnant from native vegetation.

The collected soils were thoroughly mixed and immediately stored at 4°C. Prior to the experiment, the soils were air-dried, sieved and the soil aggregates ranging from 0.5 to 1 mm diameter were used for incubation. This soil fraction was chosen for a purpose of coupling the results presented in this paper with the study on soil aggregation conducted in the companion paper (De-Campos et al. 2009). Air drying and sieving the soils did not affect the observed biogeochemical changes reported in this manuscript. A companion study (De-Campos 2006) using undisturbed soil cores from the same soils and sites where the disturbed soils were sampled, showed that the results on the measured biogeochemical parameters of the undisturbed samples were highly correlated with the results of the disturbed samples presented in this paper. Properties of the studied soils are listed in Table 1. Results on DTPA extractable Mn and Fe procedure mainly extracts chiefly free or amorphous ferrous (hydr)oxides (Loeppert and Ins-keep 1996), are reported in Table 1. Those results are used for comparison between soil extractable DTPA and soluble Mn and Fe measured in the soil solution.

Incubation and sampling method

The experiments were conducted in an anoxic biogeochemical reactor. The reactor is basically the same as described in the earlier study (De-Campos et al. 2009) coupled with a CO_2 trap system. It consisted of a modified, sealed 250 ml polyethylene centrifuge bottle with fixed pH and Eh electrodes that was connected to a CO_2 trap system. A total of 18 reactors were used in parallel in this study.

For incubation, 50 g of soil aggregates (0.5–1 mm) and 75 ml of degassed deionized-distilled Millipore® water (18 MΩ) were placed in each of the centrifuge bottles and incubated for 1, 3, 7, and 14 days under anoxic conditions. The cells were sealed immediately after the degassed water was added and CO_2-free argon (Ar) gas was flowed through the reactor continuously at a rate of 15 $cm^3 min^{-1}$. Residual CO_2 in the Ar gas was scrubbed by flowing the gas through a NaOH trap. The gas was subsequently passed though a degassed water bubbler to increase the relative humidity of the Ar gas. Under these conditions the headspace volume was recycled every 10 min. The experiments were per-formed in the dark at a temperature of 25°C (±1°C).

Redox potential (Eh) and pH values were recorded daily in the soil solution in the cells and the Eh values were corrected using the equations proposed by Rowell (1981).

Table 1 Selected soil properties of the original soils

Soil management system	Soil series	Classification	pH H$_2$O (1:1)	CEC cmolc kg^{-1}	C %	N %	Texture			NO$_3^-$
							% Sand	% Silt	% Clay	
Cultivated	Peotone (A)	Cumulic Vertic Endoaquolls	6.2	28.5	5.2	0.5	10	42	48	14.0
	Drummer (B)	Typic Endoaquolls	7.4	15.8	1.9	0.2	16	52	32	11.0
	Miami (C)	Oxyaquic Hapludalfs	6.1	13.6	0.9	0.1	18	50	32	7.0
		Average	6.6	19.3	2.7	0.2	15	48	37	10.7
Uncultivated	Drummer (D)	Typic Endoaquolls	6.7	19.2	7.6	0.6	22	50	28	36.0
	Whitaker (E)	Aeric Endoaqualfs	6.1	12.2	4.7	0.4	30	58	12	59.0
	Miami (F)	Oxyaquic Hapludalfs	5.4	11.2	3.9	0.3	36	50	14	45.0
		Average	6.1	14.2	5.4	0.4	29	53	18	46.7

Soil management system	Soil series	Classification	NH$_4^+$		K						
			Exch	Nonexch	Exch	Bray P-1	Fe	Mn	Mg	Ca
Cultivated	Peotone (A)	Cumulic Vertic Endoaquolls	2.9	2,186	234	50	145	7	728	3,687
	Drummer (B)	Typic Endoaquolls	2.5	2,164	269	87	60	4	566	2,072
	Miami (C)	Oxyaquic Hapludalfs	5.2	1,923	228	40	47	18	473	1,433
		Average	3.5	2,091	244	59	84	9.7	589	2,397
Uncultivated	Drummer (D)	Typic Endoaquolls	7.8	2,337	300	33	119	14	605	2,675
	Whitaker (E)	Aeric Endoaqualfs	11.2	2,290	190	40	64	30	300	1,496
	Miami (F)	Oxyaquic Hapludalfs	14.1	2,118	142	17	63	63	229	1,138
		Average	11.1	2,248	211	30	82	36	378	1,770

Modified from De-Campos et al. (2009)

Exchangeable K, Ca, Mg, and Na (1 M NH$_4$OAc at pH 7). Nonexchangeable K and NH$_4^+$ (NaBPh4). *CEC* cation exchange capacity (1 M NH$_4$OAc at pH 7), *C* carbon and *N* nitrogen (combustion—Leco CNH). NO$_3^-$ and exchangeable NH$_4^+$ (2 M KCl). S (monocalcium phosphate). Fe and Mn (DTPA)

Evolved CO$_2$ from the reactor was trapped by flowing the Ar gas in a series of 2 vials containing a solution of 0.07 M NaOH. The concentration of 0.07 M NaOH was chosen based on the amount of CO$_2$ evolved during the course of the 14 day experiment. The vials were replaced daily during the incubation.

After each incubation period, the centrifuge bottles were transported to an Ar-flushed glove bag and the soil solution was collected under an oxygen-free condition. Inside the glove bag, the sealed bottles were opened and 1 ml of non-filtered aliquot was removed immediately for Fe^{+2} analysis. After collecting the samples for Fe^{+2} analysis, the centrifuge bottles were sealed again under the oxygen-free conditions and centrifuged at 8,000×g for 10 min. After centrifugation, the supernatant was obtained in the glove bag using a 30 ml syringe and filtered through an Ar-gas-purged 0.45-µm filter. The supernatant was divided into three equal aliquots. Two of the aliquots were acidified using two drops of 4.5 M H$_2$SO$_4$ solution and later analyzed for nitrogen and metals. The non-acidified aliquot was analyzed for DOC.

Chemical analysis

Iron (Fe^{2+}) in the supernatant was analyzed by measuring the absorbance at 562 nm in a UV spectrophotometer (Fisher Sci. Inc. Thermo Genesis 10uv) following the method of Kirk et al. (2003). One of the acidified filtered aliquots was analyzed colorimetrically for NO$_3^-$ and NH$_4^+$ using the Quickchem 1100 system (Lachat Instruments, Milwaukee) following the methods of Wendt (1999) and Prokopy (1997), respectively. The remaining acidified filtered

aliquot was analyzed for metals (total dissolved Mn and Fe) and soluble phosphorus using inductively coupled plasma with optical emission spectroscopy (ICP-OES-Perkin Elmer Optima 2000DV, Norwalk). DOC and inorganic carbons (DIC) were analyzed using a total organic carbon TOC analyzer from the non-acidified filtered supernatant (Shimadzu TOC-Vws, USA). The samples were analyzed directly in the ICP and TOC without any further processing besides acidification. The measured concentration values of metals, phosphorus and DOC and DIC were recalculated in a soil mass basis.

The evolved CO_2 that was trapped in each of the 0.07 M NaOH vials was determined by titration with a 0.07 M HCl after adding $BaCl_2$ following the method of Zibilske (1994). Most of the evolved CO_2 was captured in the first vial and the total amount of evolved CO_2 was determined by adding the amount of CO_2 captured from each of the vials in series. Total soil carbon and nitrogen was analyzed by the combustion method using a CNH analyzer (LECO CNH 2000 Analyzer, LECO Corp., St. Joseph, MI).

More detailed data on DOC, Fe, and Mn have been presented previously by De-Campos et al. (2009) when the short-term water ponding effect on aggregate stability was quantified. Reference will be made when these results are used in this manuscript to support the current analysis.

Statistical analysis

Analysis of variance was used to determine significant effects of management systems (cultivation vs. forest), saturation duration (1, 3, 7, and 14 days), and concentration of soil organic matter on the solution chemistry of the six soils (SAS Institute Inc.). Significant effects were identified at the 5% probability level. Simple linear and Spearman's correlations were also used.

Results

Changes in Eh and pH

The changes in Eh and pH for the cultivated and uncultivated soils after incubation are shown in Fig. 1a, b. As a group, the Eh values for the uncultivated soils decreased rapidly to an average
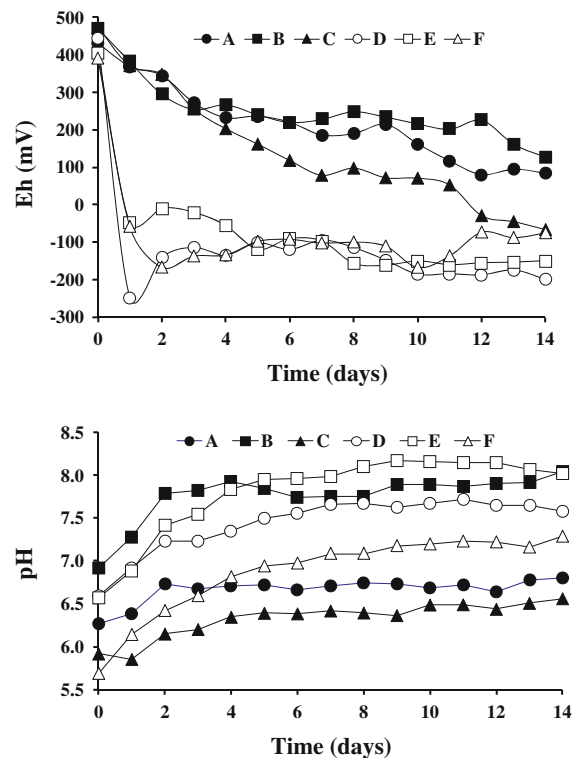
Fig. 1 a Changes in redox potential (Eh) for the averaged soils. b Trends in pH during anoxic incubation for the six soils. The soils are cultivated: (A) Peotone, (B) Drummer, (C) Miami; uncultivated: (D) Drummer, (E) Whitaker, (F) Miami. Error bars represent ± 1 SE

value of ~ -120 mV within 1 day of incubation and were stabilized to ~ -100 mV during the 14-day incubation (Fig. 1a). The response of the cultivated soils was distinct and showed a more gradual decrease in Eh from an initial value of 450 mV decreasing linearly over time to ~ 50 mV after the 14-day incubation (Fig. 1a).

Similar to the observed changes in Eh, the uncultivated soils showed a greater change in pH, with an average increase of 1.2 pH units after 14 days, than the cultivated soils that only increased 0.75 pH units for the same time frame (Fig. 1b). Unlike the rapid decrease in Eh, however, the pH changes for the uncultivated soils was more gradual.
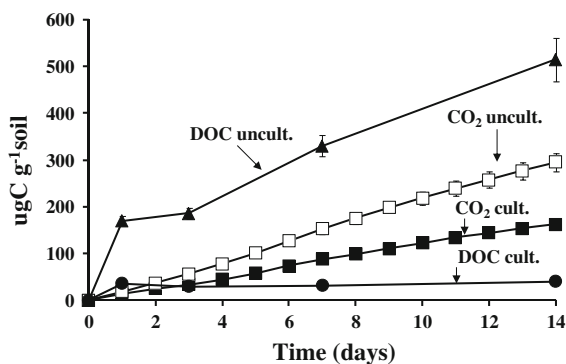
Carbon production

The cumulative amount of CO_2 evolved during the 14-day incubation for the average of each group of the three cultivated and three uncultivated soils is
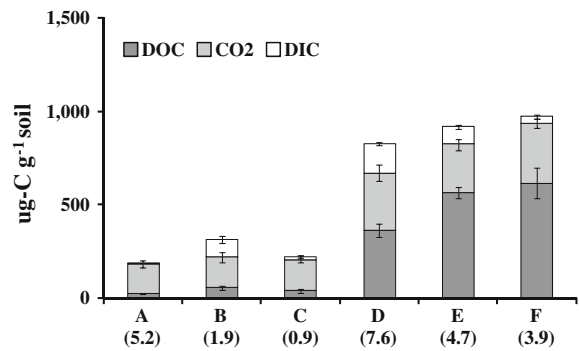
plotted in Fig. 2. On average, the amount of CO_2 evolved from the uncultivated soils was 295 ± 19 µg C CO_2 g_{soil}^{-1} after 14 days. This amount was roughly twice the CO_2 production from the cultivated soils (average of 163 ± 10 µg C CO_2 g_{soil}^{-1} after 14 days). For both types of soils, CO_2 concentration increased linearly over time indicating a fairly constant CO_2 evolution throughout the short-term anoxic incubation (Fig. 2).

The DOC concentrations are plotted in Fig. 2 for the average of each group of soils. In the uncultivated soils, the DOC concentration increased rapidly after 1 day to an average value of 170 ± 11 µg C g_{soil}^{-1} followed by a more gradual increase to 515 ± 47 µg C g_{soil}^{-1} after 14 days. The amount of carbon mobilized as DOC by the uncultivated soils was roughly 67% greater than the corresponding amount of carbon evolved as CO_2 (Fig. 2). In the case of the cultivated soils, the production of DOC was completely different with considerably less production of DOC (20% of the total amount of carbon mobilized as DOC + CO_2) relative to the amount of CO_2 evolved (Fig. 2).

The partition of DOC, DIC, and evolved CO_2 for each uncultivated and cultivated soils are shown in Fig. 3. On average, the total amount of carbon mineralized and solubilized during the 14-day incubation was 905 ± 84 µg C g_{soil}^{-1} for the uncultivated soils whereas only 240 ± 31 µg C g_{soil}^{-1} was released from the cultivated soils. The carbon solubilized as DIC was approximately the same for the two soil groups relative to the total amount of carbon released for each group of soils.
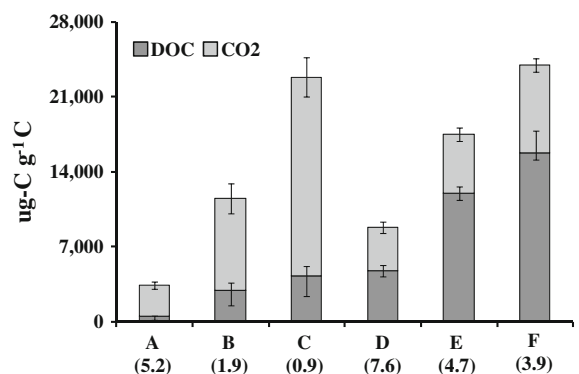

Fig. 3 Total cumulative evolved CO_2 and DOC and DIC for all soils after 14 days of incubation in a soil basis. Numbers between parentheses are the original amount of organic carbon for each soil. The soils are cultivated: (A) Peotone, (B) Drummer, (C) Miami; uncultivated: (D) Drummer, (E) Whitaker, (F) Miami. *Error bars* represent ± 1 SE

The amount of carbon mineralized and solubilized as DOC, DIC, and evolved CO_2 normalized to carbon content is shown in Fig. 4 for the six soils. As shown, less carbon was released relative to the total amount of carbon in the higher organic matter content soils than for the soils with the lower organic matter concentrations (Fig. 4; Table 1). In other words, the relative amount of carbon mobilized as DOC and evolved CO_2 normalized to carbon content increased as the carbon content for each soil decreased, as indicated by the simple linear correlations between the amount of carbon mobilized as DOC and evolved CO_2 normalized to carbon content and the percentage

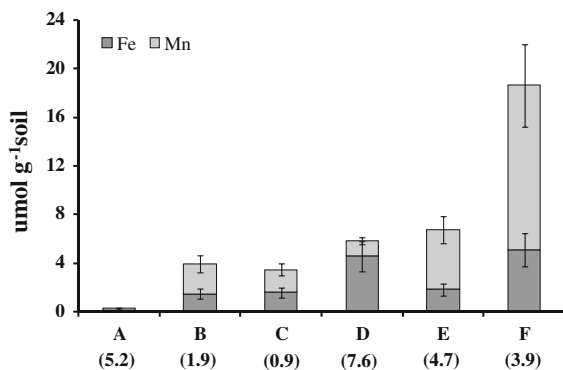Fig. 2 Trends in evolved CO_2 and DOC concentrations through time for the averaged cultivated (cult.) and uncultivated (uncult.) soils. *Error bars* represent ± 1 SE

Fig. 4 Total cumulative evolved CO_2 and DOC for all soils after 14 days of incubation in a carbon basis. Numbers between parentheses are the original amount of organic carbon for each soil. The soils are cultivated: (A) Peotone, (B) Drummer, (C) Miami; uncultivated: (D) Drummer, (E) Whitaker, (F) Miami. *Error bars* represent ± 1 SE

of carbon decomposed for each soil ($R^2 = 0.99$ for both cultivated and uncultivated soils). Similar patterns were evident for both the cultivated and uncultivated soils. This figure also shows that relative to the carbon content the amount of carbon mineralized as evolved CO_2 was larger for the cultivated soils, whereas DOC represented the largest fraction of carbon released from the uncultivated soils.

Release of metals, nitrogen, and phosphorus

The soluble iron measured as total dissolved Fe and Fe^{2+} were highly correlated and the total dissolved Fe is reported here.

The amount of total soluble Mn and Fe from each of the six soils after 14-day incubation and the carbon content of the studied soils are shown in Fig. 5. The amount of Fe and Mn in the soil solution increased for both cultivated and uncultivated soils with time of incubation, as described previously in the companion publication (De-Campos et al. 2009), and was greater for the uncultivated soils. The reduction of Fe occurred more slowly compared to that of Mn. In general, the combined dissolution of Mn and Fe was the inverse of the organic carbon content of the two soil groups, as indicated by the inverse correlations between the sum of Mn and Fe dissolution and the percentage of carbon of each soil (R^2 of 0.91 and 0.90 for the cultivated and uncultivated soils, respectively). After the 14-day anoxic incubation, there was no clear pattern between the dissolution of Mn and Fe

and the amount of DTPA-extractable Mn and Fe (Table 2). On average, the percentage of Mn dissolved during incubation compared to the DTPA-extractable Mn was greater than that observed for Fe (Table 2).

The reduction of NO_3^- occurred rapidly and within 1 day of incubation its concentration in the soil solution was below detection limits (data not shown).

The concentrations of soluble ammonium and phosphorus increased in the soil solution during incubation. Soluble ammonium concentrations are shown in Fig. 6. More ammonium was solubilized from the uncultivated soils relative to that solubilized from the cultivated soils. On average, 2.6 μmol g_{soil}^{-1} of ammonium was solubilized from the uncultivated soils after 14 days as compared to 0.2 μmol g_{soil}^{-1} from the cultivated soils. Similar to the dissolution of Mn and Fe, less ammonium was solubilized from the soils with the highest organic matter concentrations (soils A and D; Fig. 6). Mineralized ammonium increased as DOC was increased (Fig. 7). Since relatively small amounts of DOC and ammonium were solubilized from the cultivated soils (Figs. 2, 7), the positive correlation in Fig. 7 is mainly attributed to the production of DOC and ammonium from the uncultivated soils.

Soluble phosphorus from each of the six soils over the 14-day incubation is shown in Fig. 8. The pattern of soluble phosphorus from these soils was complex. The soluble phosphorus concentration from the cultivated soils is positively correlated with the production of DOC to the soil solution (Fig. 9). This pattern is not evident for the soluble phosphorus concentration from the uncultivated soils (Simple linear correlation R^2 value of 0.02).

Discussion

Both the soil solution chemistry and the amount of CO_2 mineralized to the atmosphere were strongly influenced by flooding. Increasing anoxic incubation time resulted in strongly reducing conditions with an associated increase in pH, and production of CO_2, DOC, soluble Fe and Mn, NH_4^+, and, to a lesser extent, soluble phosphorus. A clear distinction between the cultivated and uncultivated soils was observed for all of the biogeochemical parameters studied, which were significantly affected by soil

Fig. 5 Total Fe and Mn dissolved for each soil after 14 days of incubation. Numbers between parentheses are the original amount of organic carbon for each soil. The soils are cultivated: (*A*) Peotone, (*B*) Drummer, (*C*) Miami; uncultivated: (*D*) Drummer, (*E*) Whitaker, (*F*) Miami. *Error bars* represent ±1 SE

Table 2 Total Fe and Mn dissolved from the original soils after 14 days of incubation

Soil	DTPA		Solution		% of DTPA	
	Fe (mg Kg^{-1})	Mn (mg Kg^{-1})	Fe (mg Kg^{-1})	Mn (mg Kg^{-1})	Fe	Mn
A	145	7	0.71	0.71	0	10
B	60	4	8.37	4.10	14	102
C	47	18	8.98	10.39	19	58
D	119	14	25.96	7.04	22	50
E	64	30	10.46	26.64	16	89
F	63	63	29.02	74.04	46	118

Fig. 6 Changes in NH_4^+ through time for all soils. *Error bars* represent ± 1 SE
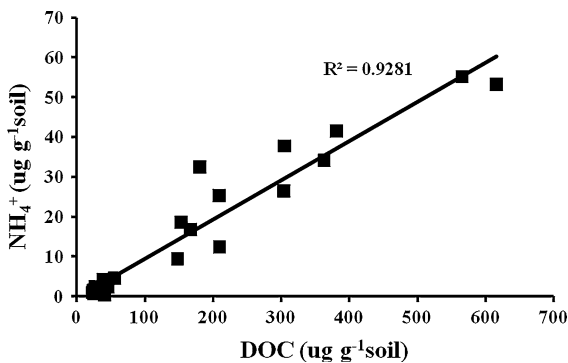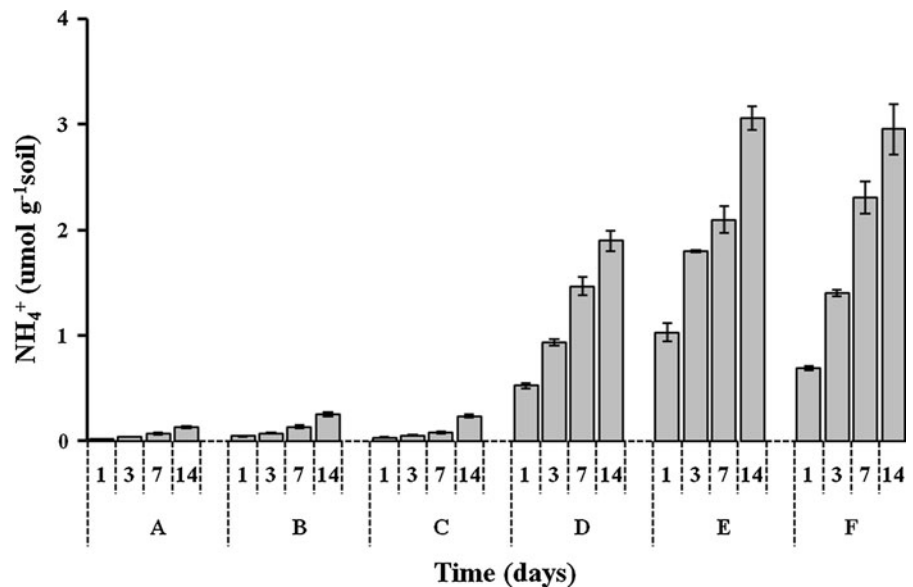
Fig. 7 Simple linear correlation between NH_4^+ and DOC. Data points are average of triplicates for each cultivated and uncultivated soil
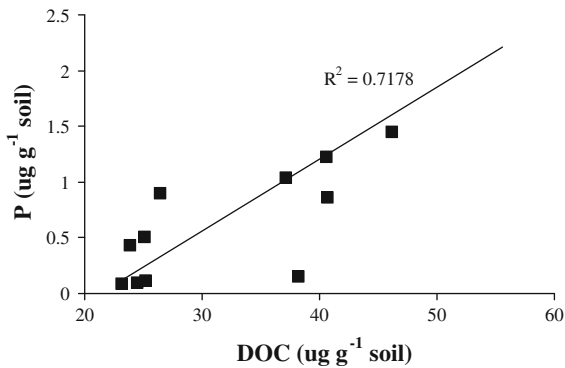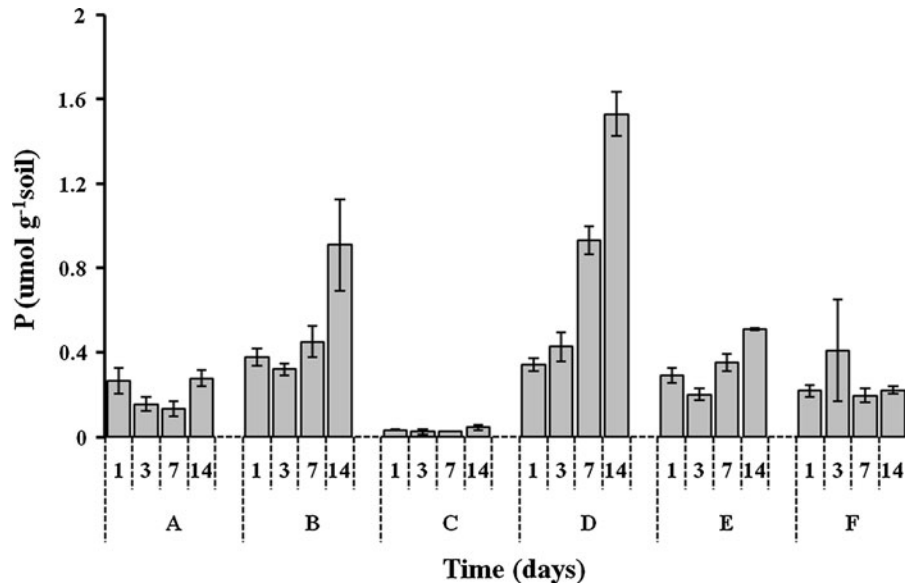
concentrations (Table 3). Another factor that could influence the observed biogeochemical changes between the six soils is the initial soil microbial population, particularly the Mn and Fe reducing organisms, which we did not measure in this study. A complementary study related to the determination of the initial soil microbial population and how it changes through time of anoxic incubation would be worthy. Overall, our results are in the range of other results reported in the literature for terrestrial and wetland soils (Table 4).

Influence of short-term saturation on redox potential and pH

A remarkable result from this study is the difference in the pathways of redox potential and pH showed by the uncultivated and cultivated soils (Fig. 1). The

management (Table 3). In contrast, Eh, CO_2, total dissolved Mn and Fe, and NH_4^+, were not significantly affected by the soil organic matter

Fig. 8 Changes in total P through time for all soils. *Error bars* represent ±1 SE

Fig. 9 Simple linear correlation between total dissolved phosphorus and DOC for the cultivated soils. Data points are average of triplicates for each cultivated soil

onset and development of strongly reducing conditions within 24 h for the uncultivated soils observed in this study (Fig. 1a), and in the companion study by

De-Campos et al. (2009) using the same soils, reactor, and similar anoxic incubation procedures; was quicker than reported in previous studies for terrestrial and wetland soils under flooding (Table 4).

One reason for the rapid drop in Eh for both the cultivated and uncultivated soils is that oxygen-free H_2O was used in the incubation experiments. In a normal field setting, some dissolved oxygen would be present in the H_2O and this would provide some residual electron acceptors in the system that would slowly be depleted. In our study, oxygen was removed from the H_2O prior to incubation resulting in a more rapid transition from oxidizing to reducing conditions. Regarding the sharp contrast between the cultivated and uncultivated soils, the underlying chemical mechanisms are not fully understood at the present time and deserve further investigation. One would conclude based upon the induction of

Table 3 Analysis of variance for the effects of soil organic matter for cultivated (S1) and uncultivated (S2) soils, management system (M), and days of anoxic incubation (D) on the measured biogeochemical variables

Source of variation	F values								
	Eh	pH	CO_2	DOC	DIC	Fe	Mn	NH_4^+	P
S1	0.90 NS	53.90*	0.02 NS	8.70*	34.33*	1.56 NS	4.23 NS	2.04 NS	26.94*
S2	1.52 NS	8.74*	0.40 NS	1.40 NS	22.78*	1.32 NS	7.79*	3.61 NS	9.85*
M	92.54*	20.41*	42.30*	160.42*	64.46*	23.75*	26.81*	269.58*	11.73*
D	5.41*	19.24*	119.45*	15.17*	8.53*	26.82*	9.53*	20.85*	4.32*

NS not significant

* Significant at $P < 0.05$

Table 4 Observed changes after 14 days of incubation and a comparison to the literature values

Measured Variables	Average Values from this Study		Range reported in Literature for Terrestrial Soils		Range reported in Literature for Wetland Soils
	Cultivated Soils	Uncultivated Soils	Cultivated Soils	Forest Soils	
Eh (mV)	50	−140	0 to 320 (a,b,c,d)[*]	300 to −120 (a,d)	510 to −250 (e,f,g,i,j,k)
pH	7.1	7.6	5.5 to 6.8 (a,b,c,d)	4.4 to 7.1 (a,d)	5.7 to 7.2 (e,f,g,j,k)
CO_2 (μmol C g_{soil}^{-1})	14	25	2 (c)	–	15 (g)
DOC (μmol C g_{soil}^{-1})	3	43	83 (c)	–	19 to 196 (e,f,k)
DIC (μmol g_{soil}^{-1})	3	8	–	–	117 (e)
Total CO_2 + DOC Carbon Mineralization (soil mass basis) μmol-C g_{soil}^{-1}	17	68	85 (c)	–	–
Total CO_2 + DOC Carbon Mineralization (normalized to carbon content) μmol-C g_C^{-1}	1,050	1,398	1,944 (c)	–	–
Mn (μmol g_{soil}^{-1})	0.1	0.7	0.1 to 1.2 (a,b)	0.1 (a)	0.12 (k)
Fe (μmol g_{soil}^{-1})	0.1	0.4	0.2 to 4 (a,b,c)	0.02 (a)	1.1 to 163 (g,j,k)
NH_4^+ (μmol g_{soil}^{-1})	0.2	2.6	–	–	0.01 to 2.2 (e,h)
P (μmol g_{soil}^{-1})	0.04	0.08	0.2 to 0.8 (b,c)	–	0.15 (e,f)

[*] References cited in the table: a—Peters and Conrad (1996); b—Scalenghe et al. (2002); c—Hutchison and Hesterberg (2004); d—De-Campos et al. (2009); e—D'Angelo and Reddy (1994); f—Phillips and Greenway (1998); g—Yao et al. (1999); h—Narteh and Sahrawat (2000); i—Zhang and Scherer (2000); j—Kirk et al. (2003); k—Grybos et al. (2007)

reducing conditions and the attendant biogeochemical changes that the nature of the organic matter in the uncultivated soils is more labile, as suggested in our earlier paper (De-Campos et al. 2009). The presence of more labile carbon sources can cause faster decrease in Eh, as reported by Hutchison and Hesterberg (2004) for a dextrose amended experiment, and that may explain the fast decrease in Eh observed in our experiment for the uncultivated soils.

The rapid onset of reducing conditions for the uncultivated soils can then be attributed to a reactive carbon component that is either absent or occluded in the cultivated soils. Agronomic practices on the cultivated soils may have changed the soil aggregates and caused the distribution of soil organic matter within aggregates being distinct from that of the uncultivated soils. The companion study about the anoxic effects on aggregation of these six studied soils (De-Campos et al. 2009) showed a more significant reduction of the aggregate stability on cultivated soils than that of uncultivated soils. In addition, it was found

that the initial concentration, nature, and solubilization of soil organic matter were important factors controlling the overall aggregate stability of these terrestrial soils after short-term flooding.

The results on redox potential (Fig. 1a) and nature of soil organic matter (De-Campos et al. 2009) suggest that the quality of soil organic matter rather than the quantity of organic matter is the main soil carbon attribute that determines rates of redox reactions in terrestrial soils upon flooding. This hypothesis is further supported by the analysis of variance that shows the redox potential was not significantly affected by the soil organic matter concentrations (Table 3).

Carbon dynamics

An important finding of this study is that the management system, along with anoxic incubation time, are major factors that determine the quantity of carbon decomposed in terrestrial soils under flooding, as shown by the analysis of variance (Table 3). The

carbon mineralization and solubilization (sum of CO_2, DOC, and DIC) was about three to four times greater for the uncultivated soils as compared to the cultivated soils (Fig. 3), despite the fact that these soils represented a wide range of soil organic carbon concentrations. This suggests that the amount of soil organic matter did not limit carbon mineralization and solubilization.

However, when the release of carbon is normalized to carbon content, the influence of the amount of organic carbon present in the soil becomes apparent (Fig. 4). In this case, a greater fraction of carbon is mineralized and solubilized from the soils with lowest organic carbon concentrations. During the 14-day anoxic incubation, 2.3% of the total carbon present was mobilized from the soil with lowest organic carbon content (Soil C; Fig. 4) against 0.1% for the soil with the highest organic matter content (Soil D; Fig. 4). This pattern suggests that soils with high organic matter concentration exhibit mobilization of a lower fraction of their total carbon concentration upon flooding than soils with low organic matter concentration.

The observed changes in DOC concentration for the uncultivated and cultivated soils were remarkable (Figs. 2, 3). We expected an increase in the DOC concentration in both soil groups as organic matter was decomposed and CO_2 production increased (Fig. 2) because this pattern has been reported by other studies and is common in soils under reducing condition (Phillips and Greenway 1998; Hutchison and Hesterberg 2004). For instance, Hutchison and Hesterberg (2004) found that most of the carbon decomposed from the silt + clay size fraction of a sandy clay loam under anoxic incubation was in the form of DOC. In their study, DOC loss after a 14-day of incubation accounted for 82% of the total carbon decomposed whereas in our study it accounts for 57 and 17% in the uncultivated and cultivated soils, respectively (Fig. 3). It is also known that the concentration of DOC produced by forest soils is higher than that of arable soils mostly due to vegetation types and concentration of organic matter (Chantigny 2003). Therefore, higher DOC concentrations in the uncultivated soils and lower but increased DOC concentration in the cultivated soils were expected. Possible explanations for what happened with the fate of DOC in those soils are as follow.

The DOC molecules in the cultivated soils consisted of high molecular weight organic molecules whereas in the uncultivated soils low molecular weight organic molecules predominated in the DOC fraction, as reported in our earlier paper (De-Campos et al. 2009). Molecules with high molecular weight are preferentially adsorbed to mineral surfaces compared with low molecular weight molecules because of their higher hydrophobicity, lower solubility, and presence of aromatic rings and carboxylic acids (Jardine et al. 1989; Gu et al. 1995; Kalbitz et al. 2000). Thus, it is likely that a large quantity of high molecular weight organic molecules generated by organic matter decomposition in the form of DOC in the cultivated soils was adsorbed by the mineral phases of those soils, and that caused the observed limited increase in DOC in the solution phase of those soils (Fig. 2).

Iron reduction has been also described as an important mechanism of dissolved organic matter (DOM) solubilization in soils under anoxic conditions because it promotes the dissolution of iron oxides thus DOM desorption (Fiedler and Kalbitz 2003). Iron reduction and dissolution was highly correlated with the increase in DOC concentration in the uncultivated soils (Spearman's correlation coefficient of 0.78) and this suggests that DOC production was affected by iron reduction in those soils.

The observed changes in DOC concentration may be also related to changes in pH. It is reported that increases in pH lead to desorption of DOC from oxide mineral surfaces (Gu et al. 1994; Kalbitz et al. 2000). The pH in the uncultivated soils increased to 7.7 after 5 days of incubation (Fig. 1b). This may have facilitated desorption of DOC from mineral surfaces and caused the observed increase in DOC production in the uncultivated soils.

In summary, it appears that DOC was more tightly adsorbed by the cultivated soils considering that these soils had higher contents of preferentially adsorbed higher molecular weight organic molecules, lower iron (hydr)oxides dissolution rates, and lower changes in pH. Thus the fate of DOC in the uncultivated soils led to a high solubilization of organic molecules whereas adsorption of soluble organic molecules was favored in the cultivated soils.

The carbon data showed here, based mainly on CO_2 and DOC, present an interesting and consistent picture of how these two groups of soils respond to flooding. During the anoxic incubation CH_4 should

have been produced as a consequence of microbial respiration and CO_2 reduction, as observed by Peters and Conrad (1996) for terrestrial flooded soils, and that could add information to further explain the cycling of carbon in those soils. Methane was not measured in this study because we were unable to trap CH_4 in our reactor and this would be of interest in a complementary study.

Nutrients cycling

Overall, the turnover of N and P compounds was greater in the uncultivated soils (Figs. 6, 7, 8, and 9). Nitrate was rapidly consumed (data not shown). It is likely that the small concentration of this compound in the original soil (Table 1) coupled with lower concentration of oxygen due to the degassing procedure adopted in this experiment were responsible for this fast consumption of nitrate.

An interesting finding of this study is the changes in ammonium concentrations. Increase in NH_4^+ concentration in the solution of soils under anoxic condition has been reported (Ponnamperuma 1972; D'Angelo and Reddy 1994) and was expected to happen in both soil groups. Such increase in NH_4^+ concentrations was observed for the uncultivated soils (Fig. 6). Conversely, the ammonium concentration in the cultivated soils did not increase with the incubation time and it seems to follow a different pathway similar to DOC (Figs. 2, 6).

Sorption mechanisms may have controlled the fate of ammonium in the cultivated soils. Fernando et al. (2005) reports that DOC can chemically react with free ammonium in solution and fix it through formation of DOC–NH_4^+ complexes that would be sorbed on soil colloids. As discussed early in this paper, the DOC was potentially adsorbed to the cultivated soils. Therefore, it is likely that the DOC molecules retained in the mineral surfaces of cultivated soils formed complexes with ammonium present in solution, in agreement with Fernando et al. (2005). The formation of these complexes would be responsible for the observed low concentration of ammonium in the solution phase of the cultivated soils.

Our results on P dissolution to the soil solution during anoxic incubation are comparable with literature data (Table 4). Prior incubation studies were focused on terrestrial soils with much higher total P concentrations

(Scalenghe et al. 2002; Hutchison and Hesterberg 2004). In these studies, more total P was dissolved during incubation (Table 4) and this was a reflection of the total amount of P present in the soil initially.

There are two possible sources of soil P dissolution during anoxic incubation. One possible explanation is due to decomposition of organic matter and that would be consistent with the production of DOC. A more likely explanation, however, is that the combined decomposition of organic matter from the soil in the form of DOC and the reducing conditions that were established during incubation, caused P dissolution in association with Fe-oxides. However, the soluble P concentrations were not correlated with the dissolution of Fe (data not shown; R^2 value of 0.26). Hutchison and Hesterberg (2004) reported that increased DOC concentration leads to increased P dissolution similarly to what we found for the cultivated soils (Fig. 9). They found a strong correlation between DRP and DOC and postulate that increases in DOM concentration from organic matter decomposition during microbial reduction induced dissolution of PO_4 by mechanisms of competitive adsorption between DOM and PO_4 for mineral surfaces. In contrast, Scalenghe et al. (2002) in a P fractionation study found that in slightly acid soils up to 80% of the total extractable P was associated with Fe and Al. Thus P dissolution in their study was strongly controlled by Fe and Al-minerals dissolution. The mechanisms that are responsible for P dissolution from our soils during anoxic incubation are not clear at present and warrant further study.

Metals cycling

Nitrate, manganese, and iron were the measured redox electron acceptors in this study. Reduction of manganese as expected occurred very early and was related to the redox state of the soil since the beginning of the experiment. The redox potential of both soil groups was in the range of 400 mV after one hour and below 400 mV after 1 day of incubation (Fig. 1a). Manganese reduction is likely in the redox range of 400 mV (Evangelou 1998) and the increase in soluble manganese concentration in soils under anoxic conditions due to reduction of manganese (IV) is extensively reported (e.g. Peters and Conrad 1996; Gao et al. 2002; Shenker et al. 2005).

Reduction of iron in soils under anoxic conditions is also well documented (e.g. Ponnamperuma 1972; Patrick and Jugsujinda 1992; Peretyazhko and Sposito 2005). In general, most of the soluble iron comes from free or amorphous iron (hydr)oxides that are reduced under redox potential below 100 mV (Ponnamperuma 1972; Petruzzelli et al. 2005). Based on the DTPA test for the whole soil (Table 2), the concentrations of soluble iron, and the range of Eh observed in this study (Fig. 1a), it is likely that most of the measured iron in our experiment came from the reduction of free or amorphous ferrous (hydr)oxides.

An interesting finding of this study was the amount of Mn and Fe dissolved from each soil after 14-day incubation that was inversely proportional to the organic carbon content of the soils (Fig. 5). This may indicate soil organic matter protecting oxide surfaces against microbial manganese and iron reduction. Thus, the microbes were unable to reduce large amount of manganese and iron in the soils with higher organic carbon content.

Concluding remarks

From our controlled reactor study, we demonstrated the complexity of biogeochemical processes associated with anoxic incubation of terrestrial soils. Reducing conditions developed very quickly and were strongly influenced by soil management. As shown, short-term flooding conditions lead to faster chemical transformations in the soils under forest and that can impact carbon budgets and the cycling of nutrients and metals.

Furthermore, the data illustrate that the soil carbon concentration alone does not determine the rates of biogeochemical transformations. We found a clear linkage between the nature of soil carbon and the production of C, N, P, Fe, and Mn from the soil during short-term saturation events. In future work a more detailed examination on N transformation, including the rapid loss of NO_3^-, the evolution of nitrous oxide along with loss of methane and possibly H_2S, and the influence of reducing organisms; would be of interest. The rapid onset of strongly reducing conditions and the concomitant changes that occur to the soil solution, point to dynamic behavior of soil organic matter.

References

Bridgham SD, Updegraff K, Pastor J (1998) Carbon, nitrogen, and phosphorus mineralization in northern wetlands. Ecology 79:1545–1561

Chantigny MH (2003) Dissolved and water-extractable organic matter in soils: a review on the influence of land use and management practices. Geoderma 113:357–380

D'Angelo EM, Reddy KR (1994) Diagenesis of organic matter in a wetland receiving hypereutrophic lake water. II. Role of inorganic electron acceptors in nutrient release. J Environ Qual 23:937–943

De-Campos AB (2006) Effects of redox on the solution chemistry and aggregate stability of Midwest upland soils. PhD Thesis, Purdue University, West Lafayette, IN

De-Campos AB, Mamedov AI, Huang C (2009) Short-term reducing conditions decrease soil aggregation. Soil Sci Soc Am J 73:550–559

Evangelou VP (1998) Environmental soil and water chemistry. Wiley, New York

Fernando W, Xia K, Rice CW (2005) Sorption and desorption of ammonium from liquid swine waste in soils. Soil Sci Soc Am J 69:1057–1065

Fiedler S, Kalbitz K (2003) Concentrations and properties of dissolved organic matter in forest soils as affected by the redox regime. Soil Sci 168:793–801

Gao S, Tanji KK, Scardaci SC et al (2002) Comparison of redox indicators in a paddy soil during rice-growing season. Soil Sci Soc Am J 66:805–817

Grybos M, Melanie D, Gruau G et al (2007) Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? J Colloid Interface Sci 314:490–501

Gu BH, Schmitt J, Chen ZH et al (1994) Adsorption and desorption of natural organic-matter on iron-oxide—mechanisms and models. Environ Sci Tech 28:38–46

Gu BH, Schmitt J, Chen Z et al (1995) Adsorption and desorption of different organic-matter fractions on iron-oxide. Geochim Cosmochim Acta 59:219–229

Hutchison KJ, Hesterberg D (2004) Dissolution of phosphate in a phosphorus-enriched ultisol as affected by microbial reduction. J Environ Qual 33:1793–1802

Jardine PM, Weber NL, McCarthy JF (1989) Mechanisms of dissolved organic-carbon adsorption on soil. Soil Sci Soc Am J 53:1378–1385

Kalbitz K, Solinger S, Park JH et al (2000) Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci 165:277–304

Kirk GJD, Solivas JL, Alberto MC (2003) Effects of flooding and redox conditions on solute diffusion in soil. Eur J Soil Sci 54:617–624

Lins HF, Slack JR (1999) Streamflow trends in the United States. Geophys Res Lett 26:227–230

Loeppert RL, Inskeep WP (1996) Iron. In: Sparks DL (ed) Methods of soil analysis. Part 3. Chemical methods, SSSA, Book Ser. 5. SSSA, Madison

Narteh LT, Sahrawat KL (2000) Ammonium in solution of flooded West African soils. Geoderma 95:205–214

Patrick WH, Jugsujinda A (1992) Sequential reduction and oxidation of inorganic nitrogen, manganese, and iron in flooded soil. Soil Sci Soc Am J 56:1071–1073

Peretyazhko T, Sposito G (2005) Iron(III) reduction and phosphorous solubilization in humid tropical forest soils. Geochim Cosmochim Acta 69:3643–3652

Peters V, Conrad R (1996) Sequential reduction processes and initiation of CH$_4$ production upon flooding of oxic upland soils. Soil Biol Biochem 28:371–382

Petruzzelli L, Celi L, Ajmone-Marsan F (2005) Effects of soil organic fractions on iron oxide biodissolution under anaerobic conditions. Soil Sci 170:102–109

Phillips IR, Greenway M (1998) Changes in water-soluble and exchangeable ions, cation exchange capacity, and phosphorus(max) in soils under alternating waterlogged and drying conditions. Commun Soil Sci Plant Anal 29:51–65

Ponnamperuma FN (1972) The chemistry of submerged soils. Adv Agron 24:29–96

Prokopy WR (1997) Determination of ammonia by flow injection analysis. In: Zellweger Analytics—Lachat instruments. Methods manual. Quickchem method 10-107-06-2-A. Zellweger Analytics, Milwaukee

Reddy KR, Patrick WH (1976) Effect of frequent changes in aerobic and anaerobic conditions on redox potential and nitrogen loss in a flooded soil. Soil Biol Biochem 8:491–495

Rowell DL (1981) Oxidation and reduction. In: Greenland DJ, Hayes MHB (eds) The chemistry of soil processes. Wiley, Chichester

Scalenghe R, Edwards AC, Marsan FA et al (2002) The effect of reducing conditions on the solubility of phosphorus in a diverse range of european agricultural soils. Eur J Soil Sci 53:439–447

Schnitzer M, Khan SU (1989) Soil organic matter. Developments in soil science, vol 8. Elsevier, Amsterdam

Shenker M, Seitelbach S, Brand S et al (2005) Redox reactions and phosphorus release in re-flooded soils of an altered wetland. Eur J Soil Sci 56:515–525

Wendt K (1999) Determination of nitrate/nitrate in surface and wastewaters by flow injection analysis. In: Zellweger Analytics—Lachat instruments. Methods manual. Quickchem method 10-107-04-1-A. Zellweger Analytics, Milwaukee

Yao H, Conrad R, Wassmann R et al (1999) Effect of soil characteristics on sequential reduction and methane production in sixteen rice paddy soils from China, the Philippines, and Italy. Biogeochemistry 47:269–295

Zhang Y, Scherer HW (2000) Mechanisms of fixation and release of ammonium in paddy soils after flooding. II. Effect of transformation of nitrogen forms on ammonium fixation. Biol Fertil Soils 31:517–521

Zibilske LM (1994) Carbon mineralization. In: Weaver RW (ed) Methods of soil analysis. Part 2. Microbiological and biochemical properties, SSSA Book Ser. 5. SSSA, Madison