



Soil organic sulfur forms and dynamics in the Great Plains of North America as influenced by long-term cultivation and climate

Jingkuan Wang^a, Dawit Solomon^{b,*}, Johannes Lehmann^b,
Xudong Zhang^c, Wulf Amelung^d

^a Shenyang Agricultural University, Dongling Road 120, Shenyang 110161, PR. China

^b Cornell University, Department of Crop and Soil Sciences, Bradfield and Emerson Hall, Ithaca, NY, 14853, USA

^c Key Lab of Terrestrial Ecological Process, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, PR. China

^d Institute of Soil Science and Soil Ecology, University of Bonn, Nussallee 13, 53115 Bonn, Germany

Received 16 September 2004; received in revised form 6 May 2005; accepted 9 July 2005

Available online 18 August 2005

Abstract

There is ample evidence about the impact of land-use and climatic variables such as temperature and precipitation on the biogeochemical cycling of organic carbon (C), nitrogen (N), phosphorus (P) in terrestrial ecosystems. However, although sulfur (S) is one of the essential nutrients for plant growth, the impact of these factors on soil organic S (SOS) forms has received little attention. The objective of this investigation was to assess the influence of long-term anthropogenic management and climate on the amount, form and distribution of SOS in bulk soils and in the clay and silt sized separates of soils from the Great Plains of North America using degradative wet-chemical reduction technique. For this purpose, samples were collected from surface soils (0 to 10 cm) of native grassland and cultivated sites along temperature and precipitation transects from Saskatoon, Canada to Texas, USA and total SOS, C-bonded S and ester-SO₄ S contents were determined. The concentration of SOS in bulk soils ranged from 194 to 853 mg kg⁻¹ soil and from 135 to 441 mg kg⁻¹ soil in the native grassland and cultivated soils, representing on the average 96% of the total soil S. Carbon-bonded S was the major organic S form comprising about two-thirds of the total SOS in clay and about three-fourth of the total SOS in silt sized separates. Only a small portion of the total SOS was present in ester linkages. Significantly larger concentration ($P < 0.05$) of SOS was found in the clay sized separates compared to the silt. Breaking of native grasslands and converting them into long-term cropping significantly reduced ($P < 0.05$) organic S in the bulk soils and in the size separates. Relatively larger proportion of SOS was lost from ester-SO₄ S (39%) than C-bonded S (25%), suggesting that it may represents the more labile form of organic S compared to C-bonded S. However, the result should be interpreted with caution since classification of organic S on the bases of bond classes may not have enough sensitivity to distinguish between labile and refractory organic S forms. The concentration of SOS ($r = -0.64^*$ and -0.79^{**}), C-bonded S ($r = -0.69^*$ and -0.83^{**}) and ester-SO₄ S ($r = -0.57^*$ and -0.76^{**}) significantly decreased ($P < 0.05$) with an increase in mean annual temperature (MAT) in bulk soils of the native grassland and cultivated sites, respectively, indicating that temperature is the most important site attribute governing turnover of SOS pool in the Great Plains of North America. Compared to MAT, the impact of precipitation on SOS forms was not pronounced in the native grassland sites. However, the

* Corresponding author. Tel.: +1 607 2551730; fax: +1 607 2551730.

E-mail address: ds278@cornell.edu (D. Solomon).

SOS loss from the bulk soils of the arable sites were enhanced significantly by an apparent increase in MAP ($r=0.54^*$; $P<0.05$) suggesting that MAP plays a key role in determining the organic S dynamics in the cultivated soils.

© 2005 Elsevier B.V. All rights reserved.

Keywords: C-bonded S; Ester-SO₄ S; HI-reducible S; Land-use change; Native grassland

1. Introduction

Sulfur (S) is a highly reactive element for which an elaborate biogeochemical cycle has evolved with intermediate exchange between atmospheric, aquatic and terrestrial phases of the environment. It is required by all biotic components as a major macronutrient necessary for formation of amino acids, enzymes, vitamins and other biomolecules, and thus plays a vital role in functioning terrestrial ecosystems (Zhao et al., 1996; Solomon et al., 2001).

Soil is the primary component of the global biogeochemical S cycle, acting as a source and sink for various S species and mediating changes of oxidation states. Sulfur in terrestrial ecosystems is found in a wide variety of inorganic and organic forms, each of which may play characteristic biological and chemical roles. Sulfate (SO₄²⁻) is the main form of inorganic S present in most soils, although some reduced S forms (e.g., elemental S, thiosulfate or sulfide) may be found in soils under predominantly anaerobic conditions (Kowalenko, 1993a; Sagggar et al., 1998). The bulk of soil S (>95%) in natural and managed ecosystems, however, is found in organic forms (Biederbeck, 1978; Janzen and Ellert, 1998; Solomon et al., 2001).

Organic components of S in soils have been the focus of several studies in the past. These studies included characterization (Frenay et al., 1970), cycling (McLaren and Swift, 1977; Strickland et al., 1987; Eriksen, 1997) and management impacts (Tabatabai and Bremner, 1972; Bettany et al., 1980; Zucker and Zech, 1985; Solomon et al., 2001) on organic S compounds in soils. In contrast, the impact of long-term cropping and climatic variables (temperature and precipitation) on the amount, form and composition of organic S compounds in soils along the temperature and precipitation transects of the Great Plains of North America has been largely neglected. Moreover, very little quantitative information is available on the influence of these variables on organic S forms in size separates (Amelung et al., 1998a), which has been

demonstrated to provide ecologically meaningful soil S pools in the tropics (Solomon et al., 2001). This is especially true in the Great Plains, where the impact of global warming may be greater than in most other parts of temperate North America (Mitchell and Mullins, 1990).

Burke et al. (1989) and Amelung et al. (1997, 1998b) reported that cultivation and climate have significant effect on soil organic matter (SOM) content of the native grassland soils from Saskatoon, Canada to Northern Texas, USA. Furthermore, in a study conducted on these soils Amelung et al. (1998a) demonstrated a significant change in total S content in bulk soils and size separates of native soils of the Great Plains as we go from cryic to hyperthermic temperature regimes. These results suggest that the different organic S constituents in the soils under investigations could be affected by changes in land-use practices and climatic variables, the extent of which, however, is not yet known.

The objective of this study was to assess the impact of long-term cultivation and climatic factors on the amount, form and distribution of organic S compounds in bulk soils and size separates (clay, <2 μm and silt, 2–20 μm) of soils selected along the temperature and precipitation transects across the Great Plains of North America. This investigation may provide a better understanding of the impact of anthropogenic management and global warming on the biochemical cycling of S as well as its interaction with the biogeochemical cycling of other elements that occur as part of complex organic polymers in SOM in natural and managed ecosystems of the Great Plains of North America.

2. Materials and methods

2.1. Site description

Soils from 18 native grassland and 17 adjacent cultivated sites (Fig. 1) were sampled in the spring

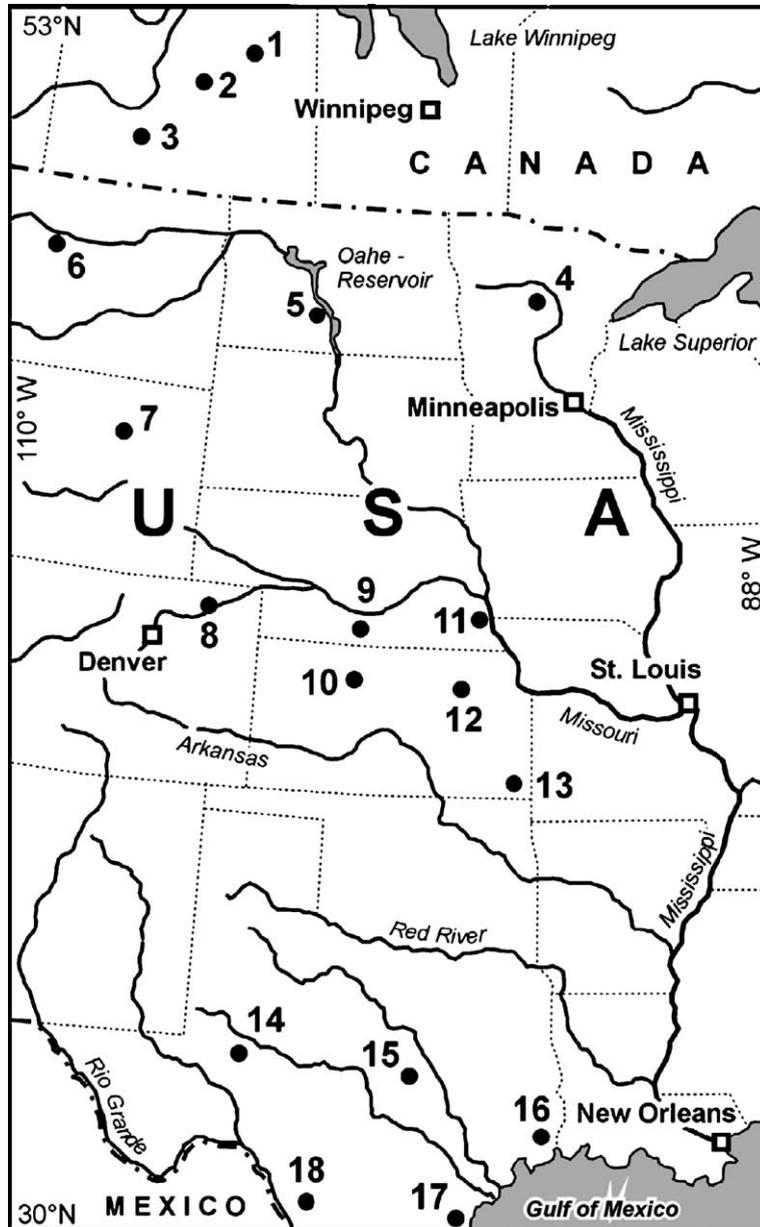


Fig. 1. Location of the study sites along the Great Plains of North America.

of 1994 along with temperature and precipitation transects (Table 1) across the North American Prairie. Most of the cultivated sites have been cropped for 60 to 83 years and they were under observation by local agricultural research stations or universities. Detailed vegetation composition, cultivation history as well as other soil characteristics of each site were

described elsewhere by Amelung et al. (1998a,b) and Sumann et al. (1998). Representative soils from each site have been previously characterized by U.S. and Canadian soil scientists (Soil Conservation Service, 1994) and latter updated according to the changes in soil taxonomy (Soil Survey Staff, 1998). Surface soil samples (0 to 10 cm) were collected from five subsites

Table 1

Location, site characteristics, particle size distribution and classification of soils from the Great Plains of North America

No. ^a	Sites	Soil series	Soil classification	MAT ^b °C	MAP ^c mm	Native soil					Cultivated soil						
						Clay %	Silt %	SOC ^d g kg ⁻¹	N %	S %	C/N	Clay %	Silt %	SOC g kg ⁻¹	N %	S %	C/N
<i>Cryic</i>																	
1	Hoey, SK	CutKife	Typic cryoborolls	0.9	456	29.1	22.3	58.2	5.3	0.73	11.0	23.4	19.4	34.8	3.3	0.51	10.7
2	Aberdeen, SK	Elstow	Typic cryoborolls	1.6	343	16.2	18.9	42.3	4.2	0.65	10.1	18.8	19.0	26.4	2.5	0.44	10.6
3	Swift Current, SK	Ardill	Typic cryoborolls	3.2	380	22.2	26.4	42.3	3.9	0.63	10.9	16.9	25.0	22.7	2.4	0.48	9.5
<i>Frigid</i>																	
4	Mandan, ND	Amor	Typic haploborolls	5.0	419	20.6	20.6	31.6	3.3	0.42	9.5	26.8	17.2	15.7	1.6	0.31	9.6
5	Havre, MT	Joplin	Aridic argiborolls	6.1	300	34.4	30.2	16.4	1.7	0.34	9.9	25.1	20.7	11.3	1.3	0.27	8.7
6	Morris, MN	Svea	Pachic udic haploborolls	6.1	565	16.5	17.1	64.0	5.3	0.89	12.0	40.3	24.8	32.7	2.9	0.45	11.1
<i>Mesic</i>																	
7	Arvada, WY	Ulm	Ustic haplargids	7.2	400	23.8	34.0	18.6	1.9	1.1	9.6	38.2	32.8	14.5	1.4	1.2	9.9
8	Akron, CO	Weld	Aridic paleustolls	10.8	375	17.7	14.9	16.9	1.6	0.27	10.2	25.6	14.5	7.7	0.88	0.24	8.8
9	Lincoln, NE	Sharpsburg	Typic argiudolls	10.9	792	32.3	27.5	40.5	3.5	0.60	11.7	36.3	23.7	19.7	2.1	0.38	9.6
10	Holdrege, KS	Holdrege	Typic argiustolls	11.6	666	24.4	22.9	29.9	3.0	0.44	9.9	21.5	21.7	13.8	1.3	0.29	10.9
11	Hayes, KS	Armo	Entic haplustolls	12.2	573	27.5	17.8	27.5	2.7	0.47	10.2	25.9	30.2	15.6	1.4	0.33	11.2
12	Manhattan, KS	Reading	Pachic argiudolls	12.4	791	33.2	26.5	30.7	2.7	0.43	11.2	32.2	15.9	15.0	1.5	0.33	10.0
<i>Thermic</i>																	
13	Parsons, KS	Parsons	Mollic albaqualfs	14.9	1000	18.2	35.5	26.8	2.4	0.40	11.3	15.5	46.7	10.1	1.1	0.23	9.5
14	Big Spring, TX	Amarillo	Aridic paleustalfs	17.1	466	20.9	7.10	11.3	1.2	0.21	9.7	11.3	2.0	4.3	0.47	0.15	9.0
15	Columbus, TX	Haletsville	Uderthic paleustolls	20.0	1030	25.1	13.6	23.7	1.9	0.39	12.4	27.3	13.4	12.9	0.99	0.26	12.9
16	Beaumont, TX	Morey	Oxyaquic argiudolls	20.3	1308	25.8	19.9	24.7	2.2	0.41	11.5	22.2	17.9	11.5	1.0	0.24	11.0
<i>Hyperthermic</i>																	
17	Alice, TX	Racombes	Pachic paleustolls	22.2	700	28.4	21.2	22.5	1.8	0.29	12.4	27.9	8.4	10.8	0.83	0.23	13.0
18	Webb County, TX	Moglia	Ustic haplocalcids	23.4	440	25.9	6.61	16.0	1.8	0.36	14.3	n. d. ^e	n. d.	n. d.	n. d.	n. d.	n. d.

^aThese numbers match the ones given in the map (Fig. 1.); ^bMAT, mean annual temperature; ^cMAP, mean annual precipitation; ^dSOC, soil organic C; ^en. d., not determined.

(200 cm³ core volume) on each of the native grassland and cultivated sites in a radial sampling scheme (Wilding, 1985), and composite samples for each site were prepared from the subsamples. The samples were air-dried and sieved (<2 mm) prior to fractionation and subsequent chemical analysis.

2.2. Physical fractionation

After removing visible root remnants, particle-size fractionation was done on <2 mm fine earth material according to Amelung et al. (1998a). Briefly, 30 g soil was ultrasonically treated with an energy input of 60 J ml⁻¹ using a probe type sonicator (Branson Sonifier W-450, Schwäbisch Gmünd, Germany) in a 1:5 (w/v) ratio. The coarse sand fraction (250 to 2000 µm) was

isolated by wet sieving. In order to completely disperse the remaining material in the <250 µm suspension, ultrasound was again applied with an energy input of 440 J ml⁻¹ in a 1:10 (w/v) ratio. The clay fraction (<2 µm) was separated from the silt (2 to 20 µm) and fine sand (20 to 250 µm) fractions by repeated centrifugation. The silt fraction was separated from the fine sand fractions by wet sieving. The clay and silt sized separates were dried at 40 °C before grinding them for chemical analysis.

2.3. Chemical analysis

The concentrations of organic C, total N and S in the samples (Table 1) were determined by C\N\H\S analyzer (Elementar GmbH, Hanau, Germany). The

analysis of the different S fractions was carried out as follows: soil solution and adsorbed SO_4^{2-} was extracted at a ratio of 1:5 (*w/v*) with KH_2PO_4 (500 mg kg^{-1} P) buffered at pH 7 to ensure effective inorganic SO_4^{2-} desorption and avoid extraction of organic SO_4^{2-} , and latter quantified by hydriodic (HI) acid reduction of SO_4^{2-} to sulfide and subsequent colorimetric determination of S as bismuth sulfide (Kowalenko, 1993a). Total soil organic S (SOS) was estimated as the difference between the total S and inorganic- SO_4S extracted by KH_2PO_4 (including water-soluble sulfate and adsorbed sulfate). HI-reducible S, consisting primarily of ester- SO_4S and inorganic- SO_4S , was analyzed by direct reduction with 4 ml of the HI acid reducing mixture and measured on a spectrophotometer according to Kowalenko (1993b). The difference between HI-reducible S and inorganic- SO_4S (KH_2PO_4 extractable) was considered as ester- SO_4S . Because HI acid will not reduce the C–S (amino acid) or C– SO_3 (sulfonate) linkage (Strickland et al., 1987), C-bonded S was considered to be that fraction of the total organic S that was not reduced by HI acid. All extractions were made on triplicate samples. Although most S speciation studies (Neptune et al., 1975; McLaren and Swift, 1977; Lehmann et al., 2001; Möller et al., 2002) were conducted in the past using air dried soils, it is worth mentioning the fact that this sample preparation procedure may have some effect on the proportions of extractable organic S and sulfate S (Watkinson and Kear, 1996; Tan et al., 1994), and thus direct comparison of results should be limited to investigations using similar sample preparation strategy.

2.4. Statistics

Bivariate and partial correlation and regression analyses were run with the standard routine of the software package SPSS 7.5 for Windows (SPSS Inc., 1997). For multiple comparisons, statistical analyses of variances were performed with the software package Statistica 6.1 (STATISTICA for Windows, 2004). For examination of statistical differences between parameters, data were analyzed by one-way analysis of variance (ANOVA) along with post hoc separation of means by the least significant difference (LSD) procedure.

3. Results and discussion

3.1. Organic S forms in the bulk soils and size separates of the Great Plains

The concentration of total organic S in surface soils (0 to 10 cm) of the native grassland and cultivated sites was shown in Table 2. According to this table, total organic S in bulk soils of the native grassland sites ranged from 194 to 853 mg kg^{-1} soil, with an average of 441 mg kg^{-1} soil (Table 2, the Arvada site is excluded), while the concentration of organic S in the cultivated soils varied from 135 to 489 mg kg^{-1} soil, the average being 300 mg kg^{-1} soil. These results also indicated that organic S was the predominant form of soil S in the Great Plains comprising on the average 96% of the total soil S. The concentration of total SOS reported in this study falls within the range reported for temperate soils by Tabatabai and Bremner (1972), Neptune et al. (1975), McLaren and Swift (1977) and Eriksen (1997). However, it is considerably lower than the values reported for humid and sub-humid tropical soils by Stanko-Golden and Fitzgerald (1991), Lehmann et al. (2001) Solomon et al. (2001) and Möller et al. (2002). The variations in organic S concentrations were likely attributed to differences in SOM levels resulting from differences in vegetation, climate and soil types.

Total organic S in the bulk soils highly significantly correlated ($P < 0.001$) with total SOC ($r = 0.97^{***}$) and N ($r = 0.97^{***}$) indicating the close association between these elements in the soils under investigation. Based on reviews of some of the earlier studies on SOC, N and S, Whitehead (1964) and Freney and Stevenson (1966) stated that the mean ratios of C/N/S for soils from various parts of the world are remarkably similar. However, unlike the conclusions of these authors, our results show considerable variations in SOC to SOS (C/S, 34 to 151) and total N to SOS (N/S, 3.0 to 7.9) ratios of the bulk soils, which may have significant implications on biogeochemical cycling of S in soils of the various ecosystems under investigation (Tables 2 and 3).

Soil organic S is a heterogeneous mixture of soil organisms and plant, animal and microbial residues, and relatively little is known about its precise form and chemical characteristics (Zhao et al., 1996; Eriksen et al., 1998; Solomon et al., 2005).

Table 2

Organic S fractions in bulk soils and two size separates of native grassland sites from the Great Plains of North America

Sites	Bulk soil					Clay					Silt				
	Organic	Ester	C-bonded	C/S ^a	N/S ^b	Organic	Ester	C-bonded	C/S	N/S	Organic	Ester	C-bonded	C/S	N/S
	S	S	S			S	S	S			S	S	S		
	mg kg ⁻¹ soil					mg kg ⁻¹ clay					mg kg ⁻¹ silt				
<i>Cryic</i>															
Hoey	696	274	422	83.6	7.6	1877 (546) ^c	657 (191)	1220 (355)	42.3	4.6	734 (164)	134 (30)	600 (134)	102.3	7.8
Aberdeen	614	243	371	68.8	6.9	2606 (422)	995 (161)	1611 (261)	36.3	4.0	773 (146)	247 (47)	526 (99)	84.1	7.9
Swift Cur.	603	243	360	70.1	6.4	1938 (430)	804 (179)	1134 (252)	39.6	4.4	584 (154)	170 (45)	414 (109)	64.7	5.6
<i>Frigid</i>															
Mandan	392	196	196	80.5	8.4	1424 (292)	643 (132)	781 (160)	50.5	5.5	487 (101)	196 (40)	291 (60)	77.4	6.7
Havre	316	109	207	51.7	5.2	1269 (209)	391 (65)	878 (145)	28.9	3.9	331 (57)	81 (14)	250 (43)	57.9	5.4
Morris	853	328	525	75.0	6.3	2044 (703)	847 (291)	1197 (412)	50.7	4.8	453 (140)	122 (37)	331 (100)	99.3	7.6
<i>Mesic</i>															
Arvada	1093	738	355	n. d. ^d	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
Akron	254	94	160	65.3	6.4	1087 (192)	320 (57)	767 (135)	37.6	4.3	371 (55)	66 (10)	305 (45)	48.4	4.2
Lincoln	566	222	344	71.5	6.1	1285 (415)	528 (170)	757 (245)	49.4	5.2	603 (166)	84 (23)	519 (143)	50.2	3.7
Holdrege	415	183	232	72.1	7.3	1438 (351)	432 (105)	1006 (246)	36.6	4.0	493 (113)	119 (27)	374 (86)	90.8	5.8
Hayes	450	204	246	61.0	6.0	1337 (368)	499 (137)	838 (231)	35.0	4.1	464 (83)	138 (25)	326 (58)	70.4	6.4
Manhattan	398	203	195	76.7	6.9	973 (323)	284 (94)	688 (229)	49.5	4.8	429 (114)	87 (23)	342 (91)	72.5	5.6
Parsons	374	118	256	72.4	6.4	1402 (255)	405 (74)	997 (181)	52.2	5.2	267 (95)	55 (20)	212 (75)	67.3	5.2
<i>Thermic</i>															
Big Spring	194	68	126	58.6	6.0	636 (133)	220 (46)	416 (87)	46.5	5.5	273 (19)	55 (4)	218 (15)	68.2	5.9
Columbus	367	121	246	64.5	5.2	908 (228)	262 (66)	646 (162)	52.9	5.2	204 (28)	76 (10)	128 (17)	109.8	6.3
Beaumont	382	139	243	64.7	5.6	1182 (305)	312 (81)	870 (224)	45.6	4.5	199 (39)	66 (13)	133 (26)	53.6	3.0
<i>Hyperthermic</i>															
Alice	271	89	182	80.5	6.5	823 (213)	329 (85)	493 (128)	64.6	5.7	343 (23)	106 (7)	237 (16)	99.5	6.3
Webb Coun.	348	136	212	73.6	5.1	781 (222)	285 (81)	496 (141)	50.0	4.0	498 (106)	182 (39)	316 (67)	78.3	4.8

^a C/S, SOC to SOS ratio; ^b N/S, total N to SOS ratio; ^c the values in the parenthesis represent S stocks (mg kg⁻¹ soil) in each size separate;

^d n. d., not determined.

One of the major limiting factors is the existing analytical approach (HI acid reduction technique) to characterize organic S fractions in soils (Prietz et al., 2003; Solomon et al., 2003, 2005). This technique differentiates SOS only in to two operationally defined fractions: C-bonded S and ester-SO₄ S, and doesn't provide information about the intermediate oxidation states of organic S forms in soils (Solomon et al., 2003). Despite such limitations, however, significant progress has been made in our understanding of organic S dynamics at the global level using this technique (Biederbeck, 1978; McGill and Cole, 1981; Zhao et al., 1996; Janzen and Ellert, 1998). Recent studies using S K-edge X-ray absorption near edge structure (XANES) spectroscopy indi-

cated that XANES spectroscopy has potentials to overcome some of the limitations of the routinely used wet-chemical S fractionation technique and could provide an opportunity to directly determine the various S oxidation states and accompanying S species in variety of geochemical samples ranging from marine sediments (Vairavamurthy et al., 1993, 1994), biosolids (Hundal et al., 2000), humic substances (Xia et al., 1998; Solomon et al., 2005) to soils (Prietz et al., 2003; Skyllberg et al., 2003; Solomon et al., 2003). However, S XANES spectroscopy requires synchrotron light i.e., electromagnetic radiation generated by particle accelerators or synchrotrons to function; and since such facilities may not be available for routine organic S characteriza-

Table 3

Organic S fractions in bulk soils and two size separates of cultivated sites from the Great Plains of North America

Sites	Bulk soil					Clay					Silt				
	Organic	Ester	C-bonded	C/S ^a	N/S ^b	Organic	Ester	C-bonded	C/S	N/S	Organic	Ester	C-bonded	C/S	N/S
	S	S	S			S	S	S			S	S	S		
	mg kg ⁻¹ soil					mg kg ⁻¹ clay					mg kg ⁻¹ silt				
<i>Cryic</i>															
Hoey	489	170	319	71.2	6.6	1740 (407) ^c	488 (114)	1252 (293)	37.3	4.1	578 (112)	111 (21)	467 (91)	93.0	7.3
Aberdeen	416	157	259	63.5	6.0	1969 (370)	655 (123)	1315 (247)	35.7	3.6	500 (95)	165 (31)	335 (64)	84.2	7.3
Swift Cur.	450	159	291	50.4	5.3	1384 (233)	529 (89)	855 (144)	35.1	4.4	569 (142)	123 (31)	446 (111)	40.2	4.9
<i>Frigid</i>															
Mandan	287	107	180	54.7	5.7	925 (248)	335 (90)	590 (158)	41.5	4.6	351 (60)	91 (16)	260 (45)	64.6	5.2
Havre	247	84	163	45.9	5.3	941 (236)	311 (78)	630 (158)	27.0	3.4	243 (50)	35 (7)	208 (43)	47.1	4.5
Morris	421	158	263	77.7	7.0	846 (341)	418 (168)	428 (172)	64.9	6.3	252 (63)	47 (12)	205 (51)	83.6	6.1
<i>Mesic</i>															
Arvada	1211	784	427	n. d. ^d	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
Akron	226	84	143	34.0	3.9	884 (226)	223 (57)	661 (169)	23.4	2.6	245 (36)	50 (7)	195 (28)	33.5	3.2
Lincoln	358	129	229	55.0	5.8	764 (277)	274 (99)	490 (178)	45.1	4.9	248 (59)	32 (8)	216 (51)	52.1	4.4
Holdrege	274	97	177	50.4	4.6	749 (161)	283 (61)	466 (100)	54.2	5.5	220 (48)	41 (9)	179 (39)	58.5	4.6
Hayes	308	115	193	50.7	4.5	699 (225)	319 (101)	380 (122)	47.8	4.1	261 (41)	71 (11)	190 (30)	60.3	3.9
Manhattan	309	106	203	48.6	4.9	943 (244)	279 (72)	664 (172)	39.7	4.2	151 (46)	35 (11)	116 (35)	71.1	6.3
Parsons	210	65	145	47.9	5.0	1025 (159)	192 (30)	833 (129)	33.4	3.6	137 (64)	31 (5)	106 (59)	32.3	3.6
<i>Thermic</i>															
Big Spring	135	41	94	31.6	3.5	548 (62)	223 (25)	325 (37)	48.7	5.1	155 (31)	49 (10)	106 (21)	43.9	3.6
Columbus	242	79	163	53.0	4.1	567 (155)	192 (53)	375 (102)	48.8	4.3	176 (24)	52 (7)	125 (17)	152.9	4.3
Beaumont	214	68	146	53.8	4.9	735 (163)	255 (57)	480 (106)	47.5	5.2	119 (21)	46 (8)	73 (13)	42.9	3.4
<i>Hyperthermic</i>															
Alice	208	60	148	51.8	4.0	521 (146)	161 (45)	360 (101)	80.5	3.9	291 (25)	94 (8)	197 (17)	150.8	4.8

^a C/S, SOC to SOS ratio; ^b N/S, total N to SOS ratio; ^c the values in the parenthesis represent S stocks (mg kg⁻¹ soil) in each size separate;

^d n. d., not determined.

tion, its use is limited only to specialized SOS studies with small number of samples.

In studies conducted using degradative wet-chemical reduction techniques Biederbeck (1978) stated that ester-SO₄ S is the dominant form of organic S in most mineral soils of temperate ecosystems, constituting between 33% and 78% of total SOS. Contrary to this conclusion, our results shown in Tables 2 and 3 indicated that most of the organic S in bulk soils of the native grassland and cultivated sites of the Great Plains was present in C-bonded S than in ester-SO₄ S form. Carbon-bonded S accounted from 49% to 68% and 62% to 71% of the total organic S, whereas ester-SO₄ S constituted for 32% to 51% and 29 to 38% of the total SOS pool in the native grassland and cultivated sites, respectively.

The only exception to these was the Arvada site which contained exceptionally high total S, SOS and ester-SO₄ S contents (Tables 2 and 3), rendering it to be a significant statistical outlier of our data base (Grubbs-test, $P < 0.01$; Hartung, 1989). Although it is the only site with Aridisols (Amelung et al., 1998a) that may contain gypsum (CaSO₄ · 2H₂O), the actual reason for the unusually high ester-SO₄ S contents in this site remained unknown. Therefore, the values for the different SOS fractions from the Arvada site were not further considered in this study.

Examination of the physically fractionated size separates indicated that significantly larger concentration ($P < 0.05$) of total SOS was present in the clay sized separates compared to the silt sized separates both in the native grassland and cultivated sites

(Fig. 2). The concentration of total organic S ranged from 133 to 703 mg kg⁻¹ soil and from 62 to 407 mg kg⁻¹ soil in the clay separates of the native grassland and cultivated sites, respectively. Relatively lower amount of total organic S (23 to 166 mg kg⁻¹ soil and 21 to 142 mg kg⁻¹ soil) was found in SOM associated with the silt separates of the native and cultivated sites, respectively (Tables 2 and 3). This was further demonstrated by the values of the enrichment factors for total SOS [$E_{SOS} = \text{SOS mg kg}^{-1} \text{ clay} / \text{SOS mg kg}^{-1} \text{ soil}$] in particle size separates of the soils under investigation, which were calculated to compare SOS concentrations by excluding the effects of different SOS levels associated with the bulk soil (Amelung et al., 1998a, data not shown). The results showed that E_{SOS} values of the size separates exhibited a highly significantly linear relation with the clay content ($r = 0.92^{***}$, $P < 0.001$) suggesting that clay content might be an additional variable to be considered for understanding organic S dynamics in the soils under investigation. The distribution of SOS among the size separates was similar to the pattern observed for SOC and N in these soils by Amelung et al. (1998a). The apparent

enrichment of SOS in the clay than in the silt sized separates could be attributed to attributed to physical and chemical stabilization of organic S as a result of (i) higher association of Fe and Al oxides and hydroxides in clay, (ii) higher reactivity and specific charge characteristics of clay minerals, and (iii) higher active surface area which enhances the enrichment of these organic compounds in clay than in silt sized separates (Solomon et al., 2003).

3.2. Effects of cultivation on organic S forms in bulk soils and size separates of the Great Plains

Breaking of virgin soils and subsequent agricultural management induces drastic change in the equilibrium status of SOS attained under undisturbed conditions, and thereby affects the quantity and quality of SOS especially in the near-surface layers (Solomon et al., 2003). This was demonstrated by the present study where significantly lower concentration of SOS was found in the bulk soils ($t = 6.3^{**}$, $P < 0.05$, $n = 16$) and in the clay ($t = 6.1^{**}$, $P < 0.05$, $n = 16$) and silt ($t = 6.3^{**}$, $P < 0.05$, $n = 16$) sized separates of the cultivated fields compared to the corresponding amounts obtained in soils of the native grassland sites of the Great Plains (Fig. 2). Our results indicate that on the average 30% of the original SOS was depleted following the conversion of the native grassland sites in to the long-term cultivated fields (Tables 2 and 3). The loss of SOS was less pronounced than the average values reported for SOC (49%) and N (46%) concentrations in these soils (Amelung et al., 1998b). The depletion of SOS was accompanied by the decrease in C/S and N/S ratios, further indicating the proportionally higher loss of SOC and N following land-use changes and suggesting that SOS is more resistant to mineralization than SOC and N in the investigated soils. The loss of organic S in the cultivated soils could be mainly attributed (i) to physical disruption of aggregates and accelerated mineralization rate of SOM as a result of increased aeration and exposure of originally inaccessible organic S to soil microorganisms (Amelung et al., 1998b) and (ii) due to reduced input of plant residue in the cultivated fields.

Considerable efforts have been devoted to characterize the source of mineralized organic S in soils. However, although several workers have observed qualitative changes in SOS forms as a result of

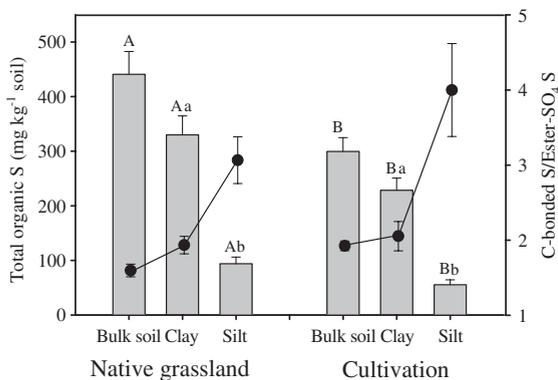


Fig. 2. Average concentrations of total organic S (bars) as well as the ratios of C-bonded S to ester-SO₄ S forms (circles) in bulk soils and size separates of the native grassland and cultivated soils of the Great Plains. The error bars represent standard errors across all samples. Capital letters (A, B and C) above the error bars indicate that total SOS concentrations between the corresponding soil fractions of native grassland and cultivated soils were significantly different, whereas, small letters above the bars for particle size separates (a and b) show significant differences between the clay and silt size fractions within one land-use system at $P < 0.05$ probability level.

cultivation, no consistent trend with regard to the interchange between the different organic S fractions is yet apparent. McGill and Cole (1981) proposed that mineralization of organic S occurs by two distinct mechanisms: (i) biological mineralization, which involves the release of S from C-bonded S as a secondary result of organic C oxidation by soil microorganisms and (ii) biochemical mineralization that involves the extracellular enzymatic hydrolysis of ester-SO₄ S due to catalysis by exoenzymes. The latter process is subject to end-product control (SO₄²⁻), and any factor that depletes soluble SO₄²⁻ should, therefore, promote biochemical mineralization. This hypothesis was also supported by observations that continual removal of SO₄²⁻, by leaching or plant uptake stimulates S mineralization (Maynard et al., 1983, 1984, 1985). In the present study, conversion of the native grassland into arable cropping resulted in significantly lower proportions of both C-bonded S ($t=4.8^{***}$, $P<0.001$, $n=16$) and ester-SO₄ S ($t=7.2^{***}$, $P<0.001$, $n=16$) in the bulk soils (Fig. 2). Following land-use changes, on the average 25% of the C-bonded S and 39% of the ester-SO₄ S were depleted from the bulk soils of the cultivated fields (Tables 2 and 3). The SOS associate with clay lost on the average 28% and 31% of the C-bonded and ester-SO₄ S, whereas the silt lost 27% of the C-bonded and 33% of the ester-SO₄ S (Tables 2 and 3). Our results indicate that on the average slightly larger proportion of SOS was lost in the form ester-SO₄ S than C-bonded S both in the bulk soils and size separates. This was also indicated by the average C-bonded S to ester-SO₄ S ratios from the native grassland and cultivated sites (Fig. 2). According to this figure, the ratio of C-bonded S to ester-SO₄ S was higher in the bulk soils and size fractions of the cultivated soils than in the corresponding separates from the native grassland sites. These results concur positively with the suggestions of Lowe (1964), McLaren et al. (1985), Schindler and Mitchell (1987) and Zhao et al. (1996) that ester-SO₄ S can be stabilized independent of the main moiety of organic matter, may represents slightly more labile organic S fraction that can serves as a readily available S pool through biochemical mineralization process. In contrast to these findings, however, other studies using incubation and field experiments (Frenay et al., 1975; McLaren and Swift, 1977; Ghani et

al., 1991; Solomon et al., 2001; Möller et al., 2002) indicated that relatively larger proportion of SOS loss following land-use changes occurs from C-bonded S than ester-SO₄ S and stated that this organic S fraction represents the major source of mineralizable S in soils supporting the suggestion by McGill and Cole (1981). This view was also supported by our previous investigation using S XANES spectroscopy where C-bonded S (SOS in highly reduced and intermediate oxidation states) forms seems to represent the more labile forms of SOS compounds compared to ester-SO₄ S (SOS in highly oxidized states) forms and the dynamics of organic S was primarily driven by SOC turnover (Solomon et al., 2003, 2005). The observed discrepancy in these studies suggests that although the conceptual model proposed by McGill and Cole (1981) provides a unifying framework for S dynamics in some ecosystems, it may not fully account the complexity of S mineralization process. It also clearly indicates that the role of C-bonded S and HI-reducible SO₄-S in S mineralization is complex and still requires further investigation. Therefore, there is a need for investigation involving an integrated use of S XANES spectroscopy and stable isotope tracer techniques to fingerprint the various organic S moieties and follow their long-term dynamics to effectively identify the source of mineralized S in the soils under investigation. The potentials of S K-edge XANES spectroscopy as a supplementary tool for understanding SOS dynamics following anthropogenic land-use changes has been recently demonstrated by Hundal et al. (2000), Prietzel et al. (2003) and Solomon et al. (2003, 2005).

3.3. Effects of climate on organic S forms in bulk soils and size separates of the Great Plains

Total organic S, C-bonded S and ester-SO₄ S in the bulk soils and size separates of the Great Plains decreased with increasing mean annual temperature (MAT). For example, the average concentration of total organic S in the bulk soils of the native grassland and cultivated sites declined in the order: cryic (638 and 452 mg kg⁻¹ soil) > frigid (520 and 318 mg kg⁻¹ soil) > mesic (410 and 281 mg kg⁻¹ soil) > thermic (314 and 197 mg kg⁻¹ soil) > hyperthermic (310 and 208 mg kg⁻¹ soil), respectively (Table 2). This was also confirmed by the significantly negative correla-

tion ($P < 0.05$) between total SOS, C-bonded S and ester-SO₄ S and MAT in the bulk soils of both the native grassland and the cultivated sites (Fig. 3). The decrease in total SOS and the different organic S fractions with an increase in MAT could be attributed to an increase in soil temperatures, which may lead to accelerated SOM decomposition and subsequent decline of organic S pool in the soils under investiga-

tion. These results concur positively with the results of Nichols (1984) and Amelung et al. (1998a), where SOC and N decreased with an increase in MAT in the Great Plains. Amelung et al. (1999) stated that differences in MAT in the Great Plains reflect not only differences in summer temperatures but also differences in length and severity of winters. According to Tables 2 and 3, compared to the southern plains (mesic to hyperthermic temperature regimes), the average concentration of organic S forms both in the bulk soils and in the size separates tend to be higher in the cryic and frigid temperature regimes of the Northern Plains, where due to the longer periods of biological dormancy, the soil freezes and the decomposition rate of SOS during the growing seasons becomes very low. On the other hand, the lower SOS level in the mesic to hyperthermic temperature regimes; where the MAT is relatively high (11 to 22 °C) and the soils hardly freeze in winter could be explained by the higher SOM turnover and organic S mineralization rather than by differences in growing season. Our results, however, differ with the results of Bettany et al. (1973), where the percentage of total S decreased as we go from Aridic Haploborall to Typic Cryoboralf in Canada.

Compared to MAT, the correlations between total organic S ($r = -0.13$ and -0.36), C bonded-S ($r = -0.08$ and -0.32) and ester-SO₄ S ($r = -0.19$ and -0.41) and mean annual precipitation (MAP) in the bulk soils were weak and not significant ($P < 0.05$) both in the native grassland and the cultivated sites, respectively. Similar trends were observed in the clay and the silt sized separates of both sites. These results indicate that the impact of MAP on organic S forms in the native grassland soils of North America was less pronounced. However, when the contents of SOS forms were related to the logarithm of the mean annual precipitation and temperature ratio ($\ln \text{MAP}/\text{MAT}$), individual r values for total organic S ($r = 0.75^{**}$ and 0.85^{**}), C-bonded S ($r = 0.72^{**}$ and 0.87^{**}) and ester-SO₄ S ($r = 0.73^{**}$ and 0.82^{**}) improved significantly ($P < 0.05$) in the bulk soils of the native grassland and the cultivated sites, respectively. These results suggest that either weak but non-significant MAP effects are still apparent or that other parameters correlating with $\ln \text{MAP}/\text{MAT}$ ratio may contribute to organic S dynamics in the soils under investigation.

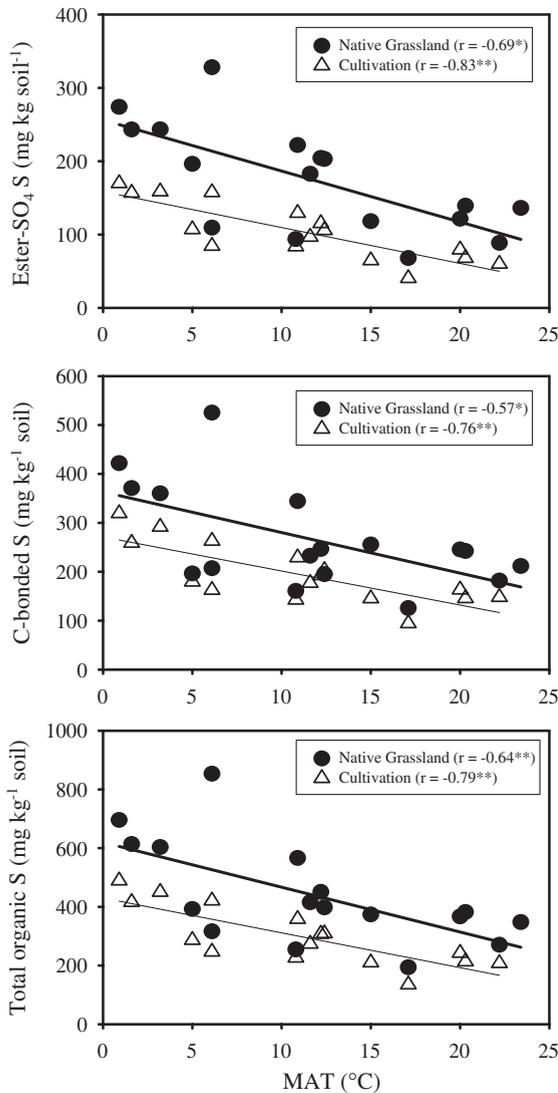


Fig. 3. Relationship between the average concentrations of total organic S, C-bonded S and ester-SO₄ S and mean annual temperature (MAT) in the bulk soils of the native grassland and cultivated sites of the Great Plains.

Since multiple regression analysis allows us to investigate and quantify the interactive impact of climatic variables and simultaneously investigate their relationship with other soil parameters such as pH and texture on organic S constituents in soils, we conducted stepwise multiple regression analysis for the different SOS forms and climatic variables (MAT and MAP) in bulk soils and size separates of the native grassland and cultivated sites. Including MAP as a multiple predictor of the SOS contents or partializing the correlations with MAT for MAP did not significantly ($P < 0.05$) improve the relationships in the bulk soils or size separates of soils collected from the native grassland sites. These results confirm that at least in the native grassland sites, the amount, composition and dynamics of SOS may not appear to be strongly related to the moisture regime and/or if the effects of MAP on SOS were apparent, they were very small to detect. However, clay content significantly improved prediction of organic S content in the bulk soils [$\text{SOS}_{\text{Native}} = 228 (107) - 17.6 (3.4) \text{MAT} + 16.99 (4.3) \% \text{clay}$; multiple $R = 0.85^{**}$, $P < 0.001$, the values in parenthesis indicating the standard errors of the regression coefficients]. The relative contribution of the variables to the prediction of total SOS contents can be estimated by the absolute value of the regression coefficients $\beta_{(X)}$ normalized to the variance of its corresponding variable X . Larger β values obtained in the present investigation for the MAT ($\beta_{\text{MAT}} = 0.74$) than for the clay content ($\beta_{\text{CLAY}} = 0.57$). These results suggest that although MAT appears to be the most important site attribute governing organic S, since the major portion of SOS in the soils under investigation was present in the clay fraction (Tables 2 and 3 and Fig. 1), clay content should be considered as an additional variable for understanding SOS dynamics in soils of the Great Plains.

In contrast to the native grassland sites, the prediction of total SOS content in bulk soils of the cultivated sites was significantly improved when MAP was included as part of the $\ln(\text{MAP}/\text{MAT})$ ratio instead of using MAT only: [$\text{SOS}_{\text{CULTIVATED}} = -310 (80) + 274 (37) \ln(\text{MAP}/\text{MAT}) + 4.2 (1.6) \% \text{clay}$; multiple $R = 0.91^{***}$, $P < 0.001$, standard error of the regression coefficients in parenthesis], with β value for clay being lower than that of the climatic variable. Our results also suggests that the SOS loss from the bulk

soils of the cultivated sites was enhanced significantly by an apparent increase in MAP ($r = 0.54^*$; $P < 0.05$), which may be ascribed to (i) the warm and moist conditions that could cause rapid decomposition of labile SOS components and S uptake by crops, and (ii) an increase in surface run-off and, accelerated water and wind erosion following land-clearing and cultivation revealing the interaction between land-use and climatic variables on the biogeochemical cycling of S in the soils of the Great Plains. Similar suggestions were put forward by Lobe et al. (2002) for the Highveld grassland agroecosystems of South Africa, where in addition to crop removal, erosion contributed to the depletion of SOC and organically bound elements in the long-term cultivated fields. Soil pH and silt content did not improve the prediction of organic S content in the bulk soils of the native grassland and cultivated sites to a considerable extent when considered both in partial and multiple regression analyses.

4. Conclusions

Carbon-bonded S was the dominant organic S form compared to ester- SO_4 S both in bulk soils and size separates of Great Plains. Similar to SOC and N, the major portion of organic S both in the native grassland and cultivated soils of was found in the SOM associated with clay sized separates.

Breaking and subsequent long-term cropping of the native grassland soils significantly decreased the concentration of total organic S, C-bonded S and ester- SO_4 S forms. Relatively larger proportion of the SOS was lost from ester- SO_4 S than C-bonded S supporting the conventional view that ester- SO_4 S, which can be stabilized independent of the main moiety of organic matter, represents slightly more labile organic S fraction that can serve as a readily available S pool through biochemical mineralization process. However, these results should be interpreted with caution since the role of C-bonded S and HI-reducible SO_4 -S in S mineralization is complex and classification of organic S fractions based only on bond classes may not have enough sensitivity to distinguish between labile and refractory organic S forms. Therefore, there is a need for further investigation involving an integrated use of S XANES spectroscopy and stable

isotope tracer techniques to effectively fingerprint the various organic S moieties and follow their long-term dynamics to effectively verify the source of mineralized S in the soils under investigation.

Climatic variables affected SOS content in both native grassland and cultivated sites. The concentration of organic S, ester-SO₄ S and C-bonded S decreased significantly with increasing MAT indicating that temperature is the most important attributes governing the turnover of SOS pool in the Great Plains. Compared to MAT, the impact of precipitation on organic S forms was less pronounced in the native grassland sites. However, an apparent increase in MAP significantly enhanced SOS loss from the bulk soils of the arable sites suggesting that MAP plays a key role in determining the organic S dynamics in the cultivated soils of the prairie. Moreover, along with climatic variables (mainly MAT); clay content could be an important soil parameter factor controlling the accumulation of organic S pools and should be considered as an additional variable for understanding organic S dynamics in soils of the Great Plains of North America.

Acknowledgments

The authors are grateful to Biederbeck, V.O., Brown, L., Brown, S., Campbell, C., Carlson, G.R., Creinwelge, G., Follett, R.F., Fryrear, D.W., Molina, R., Montemayor, E., Pruessner, E.G., Richardson, C., Schuman, G.E., Skidmore, E., Sweeney, D., Tiessen, H., Thompson, C., Towns, D., Turner, F., Vorhees, M., Vredenburg, R. and Zink, R. for their help with site location and sampling. We would like to thank Zech, W. for providing us access to the laboratory facilities at the University of Bayreuth, Germany. We wish to express our gratitude for the German Academic Exchange Service (DAAD) for providing fellowship for Wang J. (A9803245). The “Talents Program” and project “KZCX-SW-416-02” of the Chinese Academy of Sciences supported Zhang X.

References

- Amelung, W., Flach, K.-W., Zech, W., 1997. Climatic effects on soil organic matter composition in the Great Plains. *Soil Sci. Soc. Am. J.* 61, 115–123.
- Amelung, W., Zech, W., Zhang, X., Follett, R.F., Tiessen, H., Knox, E., Flach, K.-W., 1998a. Carbon, nitrogen and sulfur pools in particle-size fractions as influenced by climate. *Soil Sci. Soc. Am. J.* 62, 172–181.
- Amelung, W., Flach, K.-W., Zhang, X., Zech, W., 1998b. Climatic effects on C pools of native and cultivated prairie. *Adv. GeoEcol.* 31, 217–224.
- Amelung, W., Flach, K.-W., Zech, W., 1999. Neutral and acidic sugars in particle-size fractions as influenced by climate. *Soil Sci. Soc. Am. J.* 63, 865–873.
- Bettany, J.R., Stewart, J.W.R., Halstead, E.H., 1973. Sulfur fractions and carbon, nitrogen and sulfur relationships in grassland, forest and associated transitional soil. *Soil Sci. Soc. Am. Proc.* 37, 15–918.
- Bettany, J.R., Saggart, S., Stewart, J.W.R., 1980. Comparison of the amounts and forms of sulfur in soil organic matter fractions after 65 years of cultivation. *Soil Sci. Soc. Am. J.* 44, 70–75.
- Biederbeck, V.O., 1978. Soil organic sulfur and fertility. In: Schnitzer, M., Khan, S.M. (Eds.), *Soil Organic Matter*. Elsevier, Amsterdam, The Netherlands, pp. 273–310.
- Burke, I.C., Yonker, C.M., Parton, W.J., Cole, C.V., Flach, K., Schimel, D.S., 1989. Texture, climate, and cultivation effects on soil organic matter content in U.S. grassland soils. *Soil Sci. Soc. Am. J.* 53, 800–805.
- Eriksen, J., 1997. Sulphur cycling in Danish agricultural soils: turnover in organic fractions. *Soil Biol. Biochem.* 29, 1371–1377.
- Eriksen, J., Murphy, M.D., Schnug, E., 1998. The sulphur cycle. In: Schnug, E. (Ed.), *Sulphur in Agroecosystems*. Kluwer Acad. Publ, Dordrecht, The Netherlands, pp. 39–73.
- Freney, J.R., Stevenson, F.J., 1966. Organic sulfur transformations in soils. *Soil Sci.* 101, 307–316.
- Freney, J.R., Melville, G.E., Williams, C.H., 1970. The determination of carbon bonded sulfur in soil. *Soil Sci.* 109, 310–317.
- Freney, J.R., Melville, G.E., Williams, C.H., 1975. Soil organic matter fractions as sources of plant-available sulfur. *Soil Biol. Biochem.* 22, 1163–1165.
- Ghani, A., McLaren, R.G., Swift, R.S., 1991. Sulphur mineralisation in some New Zealand soils. *Biol. Fertil. Soils* 11, 68–74.
- Janzen, H.H., Ellert, B.H., 1998. Sulfur dynamics in cultivated temperate agroecosystems. In: Maynard, D.G. (Ed.), *Sulfur in the Environment*. Dekker, NY, USA, pp. 11–43.
- Hartung, J., 1989. *Statistik*. Oldenbourg-Verlag, Munic, Germany.
- Hundal, S.L., Carmo, A.M., Thompson, M.L., 2000. Sulfur in biosolids-derived fluvic acid: characterization by XANES spectroscopy and selective dissolution approaches. *Environ. Sci. Technol.* 34, 5184–5188.
- Kowalenko, C.G., 1993a. Extraction of available sulfur. In: Carter, M.R. (Ed.), *Soil Sampling and Methods of Analysis*. Lewis Pub., Boca Raton, FL, USA, pp. 65–74.
- Kowalenko, C.G., 1993b. Total and fractions of sulfur. In: Carter, M.R. (Ed.), *Soil Sampling and Methods of Analysis*. Lewis Pub., Boca Raton, FL, USA, pp. 231–246.
- Lehmann, J., Günther, D., Mota, M.S., Almeida, M., Zech, W., Kaiser, K., 2001. Inorganic and organic soil phosphorous and S pools in an Amazonian multistrata agroforestry system. *Agrofor. Syst.* 53, 113–124.

- Lobe, I., Du Preez, C.C., Amelung, W., 2002. Influence of prolonged arable cropping on lignin compounds in sandy soils of the South African Highveld. *Eur. J. Soil Sci.* 53, 553–562.
- Lowe, L.E., 1964. An approach to the study of the sulfur status of soils and its application to selected Quebec soils. *Can. J. Soil Sci.* 44, 176–179.
- Maynard, D.G., Stewart, W.B., Bettany, J.R., 1983. Sulfur and nitrogen mineralization in soils compared using two incubation techniques. *Soil Biol. Biochem.* 15, 251–256.
- Maynard, D.G., Stewart, W.B., Bettany, J.R., 1984. Sulfur cycling in grassland and parkland soils. *Biogeochemistry* 1, 97–111.
- Maynard, D.G., Stewart, W.B., Bettany, J.R., 1985. The effect of plants on soil sulfur transformations. *Soil Biol. Biochem.* 17, 127–134.
- McGill, W.B., Cole, C.V., 1981. Comparative aspects of cycling of organic C, N, S and P through soil organic matter. *Geoderma* 26, 267–286.
- McLaren, R.G., Swift, R.S., 1977. Changes in soil organic sulfur fractions due to the long term cultivation of soils. *J. Soil Sci.* 28, 445–453.
- McLaren, R.G., Keer, J.J., Swift, R.W., 1985. Sulphur transformations in soils using sulphur-35 labelling. *Soil Biol. Biochem.* 17, 73–79.
- Mitchell, C.C., Mullins, G.L., 1990. Sources, rates and time of sulphur application to wheat. *Sulphur Agric.* 14, 20–24.
- Möller, A., Kaiser, K., Kanchanakool, N., Aneksamphant, C., Jirasuktaveekul, W., Maglinao, A., Niamskul, C., Zech, W., 2002. Sulfur forms in bulk soils and alkaline soil extracts of tropical mountain ecosystems in northern Thailand. *Aust. J. Soil Res.* 40, 161–175.
- Neptune, A.M.L., Tabatabai, M.A., Hanway, J.J., 1975. Sulfur fractions and carbon–nitrogen–phosphorus–sulfur relationship in some Brazilian and Iowa soils. *Soil Sci. Soc. Am. Proc.* 39, 51–55.
- Nichols, J.D., 1984. Relation of organic carbon to soil properties and climate in the Southern Great Plains. *Soil Sci. Soc. Am. J.* 48, 1382–1384.
- Prietzl, J., Thieme, J., Neuhäusler, U., Susini, J., Kögel-Knabner, I., 2003. Speciation of sulphur in soils and soil particles by X-ray spectroscopy. *Eur. J. Soil Sci.* 54, 423–433.
- Saggar, S., Hedley, M.J., Phimsarn, S., 1998. Dynamics of sulfur transformations in grazed pastures. In: Maynard, D.G. (Ed.), *Sulfur in the Environment*. Dekker, NY, USA, pp. 45–94.
- Schindler, S.C., Mitchell, M.J., 1987. Dynamics of ³⁵S in horizons and leachates from a hardwood forest spodosol. *Soil Biol. Biochem.* 19, 531–538.
- Skyllberg, U., Qian, J., Frech, W., Xia, K., Bleam, W.F., 2003. Distribution of mercury, methyl mercury and organic sulphur species in soil, soil solution and stream of a boreal forest catchment. *Biogeochemistry* 64, 53–76.
- Soil Conservation Service, 1994. National Soil Characterization Data. National Soil Survey Center, NE, USA. CD-ROM.
- Soil Survey Staff, 1998. Keys to Soil Taxonomy. 8th ed. USDA, NRCS, US Gov. Print, Washington DC, USA.
- Solomon, D., Lehmann, J., Tekalign, M., Fritzsche, F., Zech, W., 2001. Sulfur fractions in particle-size separates of the subhumid Ethiopian highlands as influenced by land use changes. *Geoderma* 102, 42–59.
- Solomon, D., Lehmann, J., Martinez, C.E., 2003. Sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy as a tool for understanding S dynamics. *Soil Sci. Soc. Am. J.* 67, 1721–1731.
- Solomon, D., Lehmann, J., Lobe, I., Martinez, C., Amelung, W., 2005. Speciation of sulphur in subtropical soils: evidence from degradative wet-chemical analysis and S K-edge XANES. *Eur. J. Soil Sci.* doi:10.1111/j.1365-2389.2005.00702.x.
- Stanko-Golden, K.M., Fitzgerald, J.W., 1991. Sulfur transformation and pool size in tropical forest soils. *Soil Biol. Biochem.* 23, 1053–1058.
- Statistica for Windows, 2004. General Convention and Statistics. Version 6.1. StatSoft Incorporation, Tulsa, USA.
- Statistical Package for Social Sciences, 1997. Computer Program. Version 7.5. SPSS Inc, Chicago, IL, USA.
- Strickland, T.C., Fitzgerald, W.J., Ash, J.T., Swank, W.T., 1987. Organic sulfur transformations and sulfur pool sizes in soil and litter from a southern Appalachian hardwood forest. *Soil Sci.* 143, 453–458.
- Sumann, M., Amelung, W., Haumaier, L., Zech, W., 1998. Climatic effects on soil organic phosphorus in the North American Great Plains identified by phosphorus-31 nuclear magnetic resonance. *Soil Sci. Soc. Am. J.* 62, 1580–1586.
- Tabatabai, M.A., Bremner, J.M., 1972. Forms of sulfur and carbon, nitrogen and sulfur relationships in Iowa soils. *Soil Sci.* 114, 380–386.
- Tan, Z., McLaren, R.G., Cameron, K.C., 1994. Forms of sulfur extracted from field moist, air-dried and conditioned soils. *Aust. J. Soil Res.* 32, 832–834.
- Vairavamurthy, A., Manowitz, B., Luther III, G.W., Jeon, Y., 1993. Oxidation state of sulfur in thiosulfate and implications for anaerobic energy metabolism. *Geochem. Cosmochim. Acta* 57, 1619–1623.
- Vairavamurthy, A., Zhou, W., Eglinton, T., Manowitz, B., 1994. Sulfonates: a novel class of organic sulfur compounds in marine sediments. *Geochem. Cosmochim. Acta* 58, 4681–4687.
- Watkinson, J.H., Kear, M.J., 1996. Sulfate and mineralizable organic sulfur in pastoral soils of New Zealand: II. A soil test for mineralizable organic sulfur. *Aust. J. Soil Res.* 34, 405–412.
- Whitehead, D.C., 1964. Soil and soil–plant nutrition aspects of the sulphur cycle. *Sol Fert.* 27, 1–8.
- Wilding, L.G., 1985. Spatial variability: its documentation, accommodation and implication to soil survey. In: Nielsen D.R., Bauma, J. (Eds.), *Soil Spatial Variability*. Proceedings of ISSS and SSSA, PUDOC, Wageningen, The Netherlands, pp. 166–194.
- Xia, K., Weesner, F., Bleam, W.F., Bloom, P.R., Skyllberg, U.L., Helmke, P.A., 1998. XANES studies of oxidation states in aquatic and soil humic substances. *Soil Sci. Soc. Am. J.* 62, 1240–1246.
- Zhao, F.J., Wu, J., McGrath, S.P., 1996. Soil organic sulphur and its turnover. In: Piccolo, A. (Ed.), *Humic Substances in Terrestrial Ecosystems*. Elsevier, Amsterdam, The Netherlands, pp. 467–506.
- Zucker, A., Zech, W., 1985. Sulfur status of four uncultivated soil profiles in northern Bavaria. *Geoderma* 36, 229–240.