Characteristics of Soil Water-Soluble Organic C and N Under Different Land Uses in Alaska

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Abstract: Land use conversion induces quantitative change of soil water-soluble organic matter (WSOM), but knowledge of such change is still limited. In this study, field moist and air-dried soils sampled from subarctic Alaska under three land use managements (i.e., forest, agriculture, and grassland converted from agricultural use and under a Conservation Reserve Program [CRP]) were extracted with deionized water and separated by filtration into different size fractions (2.5 μm, 0.45 μm, and 1 kDa). Water-soluble organic C (WSOC), water-soluble organic N, and fluorescence spectroscopy of each fraction were determined. There were few differences in quantitative data between samples from different land uses with air-dried samples, implying that air-dried samples were not suitable for characterizing the impact of soil management practices on soil WSOM. For field moist soil samples, the WSOC contents decreased in the order forest > CRP > agricultural land. Furthermore, WSOC was dominated by large (>0.45 μm) and small (<1 kDa) size molecules in CRP and forest soils, whereas small molecules predominated in agricultural soils. The WSOM of different size fractions and land use displayed three similar fluorophore components (two humic-like and a tyrosine-like), indicating that the impact of land use was mainly on the quantity, rather than on the composition, of WSOM. In conclusion, our data suggested that the long-term agricultural land use could lower the WSOM levels in soils; however, the decreasing trend could be reversed by conversion of agricultural land to grassland under conservation.

Key words: Water-soluble organic matter, size fraction, field moist soil sample, air-drying process, fluorescence excitation/emission matrix, Humification Index.

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Soil water-soluble organic matter (WSOM) is the most labile and mobile form in soil organic matter pools (Zsolnay, 1996; Boyer and Groffman, 1996). Soil WSOM serves as a potential nutrient source to soil microorganisms and plants, facilitates transport of metals and organic contaminants through soils, and regulates the production of greenhouse gases such as CH_4 and N_2O (Zsolnay, 1996; Temminghoff et al., 1997; Lu et al., 2000; Marschner and Kalbitz, 2003; Jones et al., 2004; McDowell et al., 2006). Terrestrial WSOM is also an important source of dissolved organic matter in aquatic ecosystems, which affects water quality (Mulholland, 1997; Quall and Richardson, 2003; Yu et al., 2003).

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Soil SWOM is a mixture of compounds of various molecular sizes. Although the importance of soil WSOM has been recognized, the information on sizes of WSOM and its properties is still lacking and inconsistent. An example of such inconsistence is that two different sizes (0.45 and 2.5 μm) are used for separation of particulate organic matter from WSOM (Zsolnay, 2003; Chantigny et al. 2010). For mobility, general knowledge is that small-size WSOM are more mobile than the large ones (McCarthy, 1996; Gu et al., 1996; Zhang et al., 2011). Regarding biodegradability of different size fractions of WSOM, most of the information is from freshwater or seawater but not from soil. Yamashita and Tanoue (2004) reported that large-size fractions of dissolved organic matter are least degradable in surface ocean water. In contrast, Amon and Benner (1996) reported that large-size compounds are readily used by microbes in aquatic ecosystems.

Sequential filtration has been used to determine the relationship between WSOM size and biodegradability (Delprat et al., 1997; Smolander and Kitunen, 2002; Kiikkilä et al., 2006). These size fractions include less than 1 kDa, 1 to 10 kDa, 10 to 100 kDa, and more than 100 kDa. In these three studies, two were in forest soil (Smolander and Kitunen, 2002; Kiikkilä et al., 2006), and one was on land conversion from forest to maize field (Delprat et al., 1997). Size fractions are often used in freshwater and seawater studies for dissolved organic matter (DOM). In the freshwater/seawater studies, less than 1 kDa is referred to as low-molecular dissolved organic matter (DOM) and more than 1 kDa but less than 0.45 μm DOM as high-molecular DOM. Soil is the major source of terrestrial DOM in water ecosystems. For most studies for soil WSOM, air-dried soil samples are used. The air-drying process alone affects the quantity of soil WSOM. The amount of WSOM from air-dried soil samples is three- to 10-fold higher that from field moist soil samples (Jones and Willett, 2006). However, the WSOM fraction that is increased by the air-drying process is not known.

Fluorescence spectroscopy is used to characterize DOM or soil WSOM (Ohno and Bro, 2006; Embacher et al., 2008; Ohno et al., 2009; Zhang et al., 2011). Using parallel factor analysis (PARAFAC) to decompose fluorescence excitation-emission matrix (EEM), fluorophore components and their relative distribution in soil WSOM can be recognized (e.g., humic-like, fulvic-like, tryptophan-like, and tyrosine-like fluorophores). In addition, the Humification Index (HIX) from fluorescence spectroscopy is used to evaluate the degree of humification of soil WSOM (Zhang et al., 2011).

For soil WSOM, land use affects WSOM concentration and types of WSOM. Clear cutting of forests can increase downward movement of soil Fe and Al chelated with humic acids generated in the surface mineral soil (Hughes et al., 1990). When forest soil is converted to agricultural soils, fulvic acid becomes dominant in mineral soil as WSOM (Delprat et al., 1997). The studies in high latitude often focus on impact of land use on total soil carbon storage (Grünzweig et al., 2003; 2004) or on effect of vegetation on WSOM in tundra forest

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soils (Neff and Hooper, 2002). Little information is available on WSOM for different land uses in the high-latitude areas. High-latitude areas are sensitive to climate change. Enhanced organic matter decomposition in soil and land use changes because of climate change (Juday et al., 2005) will inevitably affect soil WSOM. In the other studies in the temperate regions, an increase in agricultural activities can significantly increase the delivery of nutrients such as N to fluvial ecosystems (Wilson and Xenopoulos, 2009). As such, understanding current soil WSOM in subarctic regions under different land uses will provide information for future land and water quality management. The working hypothesis of this study was that the quantity and composition of WSOM could be affected by land use management. To verify this hypothesis, this study (i) quantified water-soluble organic carbon (WSOC) and water-soluble organic nitrogen (WSON) of soil samples from three land uses (i.e., forest, agriculture, and grassland converted from agricultural use and under a Conservation Reserve Program [CRP]), (ii) determined if air-drying process affected soil WSOM concentration and its size distribution, and (iii) characterized fluorescence properties of WSOM from field moist and air-dried soil samples.

MATERIALS AND METHODS

Site Description

The study sites are located in Delta Junction area of Alaska (64°49′N, 147°52′W). The area has a boreal forest ecosystem that is characterized by long cold winters and short cool-to-mild summers. The average low temperature in January is −23°C. The average high temperature in July is +20°C. Average air temperature (1980–2008) in the study area is −1.6°C. The average precipitation of 29-year period (1980–2008) is about 298 mm per year. Three sites were selected in the area. Each site consisted of three land use units: forest, CRP, and agricultural land. Soil in all three sites is Volkmar series of Aquatic Haplocryepts developed from micaceous silt loess overlying sand and gravel outwash materials (NRCS, 2012). The surface mineral soil usually has a silt loam texture with pH ranges from 4.8 in the surface horizon to 5.4 in B horizon. For the three study sites, Site 1 was 2.3 km northwest of Site 2, and Site 3 was 1 km south of Site 2. The native forest in these three locations is primary blank spruce (*Picea mariana*), birch (*Petula Neoalaskana*), and poplar (*Populus trichocarpa*), with forest floors consisting of a thick layer of mosses. In 1978, part of the native forest was converted to agricultural land. Since then, the agricultural land has been under continuous barley (*Hordeum valgare* L.) with conventional tillage (disked in each spring). In 1992, part of the agricultural land was converted into grassland through the CRP administrated by the US Department of Agriculture (Osborn et al., 1992). The CRP land has a mixture of shrubs, forbs, and grasses. By the time of soil sampling in fall 2005, all CRP land had a history of 13 years after conversion from agricultural land. In all three sites, no lime was applied in all land uses.

Soil Sampling

The forest soil had a thick organic layer that was clearly different from mineral soils. To have a consistent comparison among soils of the three land uses, we only considered mineral soils in this study. Soil samples were taken in September 2005 using a 15.25-cm (diameter) core before the first snow. Depth of surface soil organic matter was measured for each sampling core and then separated from mineral soils. The sampling depth of mineral soils was 0 to 10 cm. Three replicated samples were taken from each land use unit of each site, and each sample was a composite of three cores. The fresh samples were sieved through a 2-mm screen and stored in a refrigerator (4°C) for further use in analysis. Soil chemical and physical properties of the three land uses were reported by Zhang et al. (2012). In brief, the soil from agricultural use has a lower bulk density (0.67 Mg m^{-3}) than that of CRP (0.73 Mg m^{-3}) and forest (0.83 Mg m^{-3}) soils. Total organic C and N in the agricultural soils are total C = 60.4 ± 19.5 g kg^{-1} soil, total N = 3.2 ± 1.1 g kg^{-1} soil; in the forest soil are total C = 42.5 ± 9.3 g kg^{-1} soil, total N = 1.9 ± 0.5 g kg^{-1} soil; and in the CRP soil are total C = 49.4 ± 7.5 g kg^{-1} soil, total N = 2.5 ± 0.5 g kg^{-1} soil. Soil pH was approximately 5.3 for all three soils.

Extraction and Fractionation of WSOM

Field moist and air-dried soil samples, each with three replicates, were used for extraction and fractionation of WSOM. Controls of three replicates with no soils were set up and operated in analysis in the same way as the soil samples. In brief, deionized (DI) water (300 mL) were added to 30.00-g (oven-dried base) soil samples in a 500-mL Nelgene plastic bottle (soil-water ratio, 1:10 wt/vol). For the field moist soil samples, 300 mL of water was added to the bottle including the volume of the water already in the moist soil samples. The bottles were shaken for 30 min on an Eberbach 6000 reciprocal shaker (Eberbach Corporation, Ann Arbor, MI) at room temperature (22°C ± 1°C) followed with centrifuging at 900*g* for 30 min with an Eppendorf 5810R centrifuge (Eppendorf North America Inc., Hauppauge, NY). After centrifugation, the supernatant was filtered through a 2.5-μm filter (Whatman No.42, Ashless Filter; Whatman International Ltd., Kent, UK). A portion (~100 mL) of the filtrate was saved for analysis of total organic C, organic N, NH_4-N, and NO_3-N concentrations and fluorescence properties. The remaining portion (~200 mL) was filtered with a 0.45-μm filter (GN-6; Pall Corporation, Port Washington, NY). The 0.45-μm filtrate was then divided into two portions: one (~100 mL) was for analysis of total organic C, organic N, and mineral N concentrations and fluorescence properties and the other was further filtered with a 1-kDa membrane. The 1-kDa ultrafiltration was performed under 55 psi pressures with an Amicon 8050 stirred cell system with 1-kDa membranes (Millipore Regenerated Cellulose YM1; Millipore Corporation, Bedford, MA).

Before each size fractionation, both 2.5- and 0.45-μm filter membranes were rinsed three times with DI water to remove any soluble C. To remove any soluble C or N in 1-kDa membranes, the 1-kDa membranes were placed in 200 mL 5% NaCl for 30 min. After that, the 1-kDa membranes were floated in DI water in a 250-mL glass beaker with glossy face down for at least 1 h. During this 1 h, DI water was changed three times about 15 min each. Then, the membrane was placed in the Amicon system and rinsed with DI water for three times at 55 psi with 200 mL each. To check if the filter membranes contained any water-soluble C and N, the final rinse solutions were collected for analysis of water-soluble C and N concentrations before solution sample filtration. The difference of water-soluble C and N between filtered water and pure DI water were compared, and no difference was found ($P > 0.05$).

Solution Total C, Total N, and Mineral N Analysis

Concentrations of inorganic C, total C, and total N in solution samples were determined using a Shimadzu TOC-V Organic Carbon and Total Nitrogen Analyzer (Shimadzu Scientific Instruments Inc., Columbia, MD). Ammonium (NH_4-N)

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and nitrate (NO_3-N) in solution samples were measured on an Astoria ALPKEM AutoAnalyzer (Astoria-Pacific International, Clackamas, OR).

Concentration of WSON was calculated by subtracting mineral (NH_4-N + NO_3-N) N from total N in filtrates. The concentrations of WSOC and WSON in the more than 0.45-μm fraction were obtained by subtracting less than 0.45-μm fraction from less than 2.5-μm fraction. The WSOC and WSON concentrations in the 1-kDa to 0.45-μm fraction were obtained by subtracting less than 1-kDa fractions from less than 0.45-μm fraction.

Fluorescence Spectroscopic Analyses and PARAFAC Modeling

Fluorescence EEM for solution samples of each fraction was measured using a FluoroMax-4 spectrophotometer (Horiba Jobin Yvon Inc., Edison, NJ) equipped with a 150-W ozone-free xenon lamp as the excitation source. Before determination, samples were diluted to avoid an inner filter effect by adding Milli-Q water (Milli-Q System, Millipore Corporation) so that the UV light absorbance of solutions at 240 nm was approximately 0.1 using a UV-VIS-NIR spectrophotometer UV-3600 (Shimadzu Scientific Instruments Inc.). The diluted samples were used for the determination of fluorescence EEM. The excitation wavelengths were ranged between 240 and 400 nm. The emission wavelengths ranged 300 to 500 nm. The increment of excitation and emission wavelengths was 3 nm. Excitation and emission slits were set at a 5-nm band width with an integration time 0.1 sec. Using files created by the manufacturer, sample EEM were corrected for instrument bias and Rayleigh scatter lines were masked. The final EEM for samples were obtained by first subtracting the controls (average of three replicates) to remove Raman scatter effects (Christensen et al., 2005) and then was normalized using the area from the Milli-Q water Raman peak at an excitation wavelength of 350 nm (Determann et al., 1994). In addition, when the emission wavelength was less than the excitation wavelength (a physical impossibility), the value was set.

Fluorescence EEM were separated based on land uses and size factions. The separated EEM were analyzed by PARAFAC models. Briefly, fluorescence EEM were loaded into software Matlab (Version 7.1, The MathWorks Inc., Natick, MA). The PARAFAC analysis was conducted using Nway toolbox in the Matlab. The contours of samples were first plotted with the Matlab. Then, a nonnegativity constraint was applied to restrict negative fluorescence intensities that were chemically impossible. Two to five components were fitted to the data to investigate the correct number of components. Core consistency (close to 100% is optimal) was used to assess the proper number of components for PARAFAC models (Bro and Kiers, 2003; Ohno and He, 2011). Contour plots and fluorescence intensity of each component were produced by PARAFAC model. The relative loading of each component was calculated as the percentage of total components.

Fluorescence HIX was calculated as the ratio of the summation of fluorescence intensity from emission wavelengths of 450 to 480 nm (high quartile) to that of 300 to 345 nm (low quartile) (Zsolnay et al., 1999).

Data Analysis

The effects of CRP, forest, and agricultural soils on parameters (mineral N, WSOC, and WSON) at each size fraction (<1 kDa, 1 kDa–0.45 μm, and >0.45 μm) were analyzed with one-way analysis of variance using Statistix 8 (Analytical Software, Tallahassee, FL). Similarly, the size difference within each land use; mineral N, WSOC, and WSON under each land use; relative loading of fluorescence components; and fluorescence intensity of high quartile, low quartile, and HIX were statistically analyzed (analysis of variance). Mean comparisons were determined by least significance difference tests at $P \leq 0.05$. For comparison of the field moist with air-dried soil samples, student t test was used. In this study, all results were based on oven-dry weight of soil (105°C for 24 h).

RESULTS AND DISCUSSION

Water-Soluble C and N

The statistically different ($P \leq 0.05$) WSOC concentrations in field moist soil samples in decreasing order were 244 mg kg^{-1} in forest soil, 186 mg kg^{-1} in CRP soil, and 163 mg kg^{-1} in agricultural soil (Table 1). Air-drying increased the WSOC concentration in all three soils to about 400 mg kg^{-1}. However, the difference in the WSOC concentrations among the air-dried soil samples of the three land uses decreased; that is, the WSOC levels in all three types of air-dried soils were not statistically significantly different ($P > 0.05$). The WSON concentrations were much lower than WSOC concentration in a range around 10 mg kg^{-1}. In contrast to WSOC, there were no statistical differences ($P > 0.05$) among land uses for WSON for the field moist soil samples, but WSON became marginally statistical differences ($P = 0.07$) among land uses for the air-dried soil samples. Air-drying process only increased WSOC but not WSON except for the CRP soils (Table 1). Consequently, C/N ratio of water soluble organic matter for air-dried soil was higher than that of the field moist soil samples. Our observations are partially consistent with those of Jones and Willett (2006) who reported that air-drying soil samples

TABLE 1. WSOC and WSON (<2.5 μm) in Field Moist and Air-Dried Samples From CRP, Forest, and Agricultural Soils

	WSOC, mg kg^{-1} of dry soil		WSON, mg kg^{-1} of dry soil		C/N Ratio	
Land Use	Field Moist	Air-Dried	Field Moist	Air-Dried	Field Moist	Air-Dried
CRP	186.36	453.81*	11.84	13.12*	15.74	34.60*
Forest	243.92	446.18*	9.88	8.26 NS	24.69	54.03*
Agricultural	162.51	388.24*	14.86	13.47 NS	10.93	28.83*
P (F test)	0.005	0.56	0.52	0.07		
LSD (0.05)	47.17	NS	NS	4.86		

Values are means of nine replicates. Statistical analysis was applied to the indexes among different land uses, except for C/N of WSOM.

*Data of air-dried samples significantly different from the corresponding data of field moist samples at $P \leq 0.05$.

LSD, least significance difference; NS, not significant at $P = 0.05$.

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TABLE 2. Size Distribution of WSOC and WSON in the Field Moist Soil Samples From CRP, Forest, and Agricultural Land Uses

	WSOC, mg kg^{-1} of dry soil				WSON, mg kg^{-1} of dry soil				C/N Ratio		
Land Use	L	M	S	Impact	L	M	S	Impact	L	M	S
CRP	68.94	10.06	107.36	L ~ S > M	8.36	0.52	3.02	L > M ~ S	8.25	19.41	35.50
Forest	88.71	8.26	146.95	L ~ S > M	7.59	0.35	1.94	L > M ~ S	11.69	23.67	75.76
Agricultural	36.41	7.20	118.90	L ~ M < S	4.26	1.12	9.94	L ~ M < S	8.55	6.44	11.96
P (F test)	0.35	0.56	0.32		0.42	0.02	0.002				
LSD (0.05)	NS	NS	NS		NS	0.53	4.31				

Values are means of nine replicates. Statistical analysis was applied to WSOC and WSON among different land uses within each size fraction. For size comparison within the same land use: ~, statistically not significant at $P = 0.05$; > or <, significantly higher or lower with least significance difference (LSD) ($N = 9$, $P \leq 0.05$). Significance test was not applied to C/N ratios.

L, large-size fractions (>0.45 μm); M, medium-size fractions (1 Da–0.45 μm); NS, not significant at $P = 0.05$; S, small-size fractions (<1 kDa).

resulted in a three- to 10-fold increase in both WSOC and WSON concentrations in the air-dried as compared with field moist soil samples. Haynes (2000) reported that the concentrations of WSOC, WSON, and WSOP were much greater when extracted from air-dried than from field moist soils. This difference was proportionately greater for soils with higher total soil organic matter contents. Haynes (2000) proposed that WSOM in air-dried soils originated from soil solution, from lysed desiccated microbial cells, and from labile humic material. Thus, we assume that the lysis of the microbial pool and release of humic materials could be the two major mechanisms of the increase of WSOC by air-drying in our study.

Most studies have shown that WSOM or dissolved organic C (DOC) is higher in forest than in agricultural soils (Chantigny, 2003). Only a few studies have shown that WSOM is higher in agricultural than in forest soils (Boyer and Groffmann, 1996; Quideau and Bockheim, 1997). Nearly all these studies were conducted in temperate regions, where soil ecosystems include large fauna such as earthworms. In contrast, soil ecosystems in subarctic Alaska are characteristically lacking in large fauna activities, resulting in stratifications of soil organic matter in the forest soils (a large quantity of semidecomposed organic matter accumulated on soil surface) (Zhang et al., 2012). However, such stratification of organic matter appeared not to be affected by the WSOC in forest mineral soil because its WSOC was statistically greater than that of the agricultural and CRP soils in the field moist soil samples (Table 1). Our results also showed that land use change from forest to arable land did result in a decrease in WSOC in the field moist soil samples but not in air-dried soil samples. Other reports have shown that there is a high WSOM in agricultural soil resulting from a flush of WSOM after land conversion from forest to agriculture (Meyer and Tate, 1983; Moore, 1989). However, the reported WSOM flush after land use change from forest to agriculture is 2 to 10 years, but the history of land use change from forest to agriculture in our study was much longer (~27 years) than 2 to 10 years. Thus, our data suggested that, after the flush period, the long-term agricultural land use could lower WSOM levels in soils. The positive observation is that the decreasing WSOM could be reversed by conversion of agricultural land to grassland under conservation. Previously, Haynes (2000) demonstrated that inclusion of grazed pastures in a cropping system can maintain labile organic C in higher amounts than is possible under annual cropping.

Molecular Size Distribution of Water-Soluble C and N

Three different molecular size fractions were separated: small molecules, less than 1 kDa; medium molecules, 1 kDa to 0.45 μm; and large molecules, less than 2.5 μm but more than 0.45 μm. The concentration of WSOC within each size fraction was rather similar among soils of the three land uses for both field moist and air-dried samples (Tables 2, 3). Comparing the two sets of data in Tables 2 and 3, we found that the WSOC concentrations decreased in the large-size fractions but increased in the medium- and small-size fractions of WSOC in all three soil sample types by air-drying. In contrast, the WSON was statistically different ($P < 0.05$) in medium (1 kDa–0.45 μm) and small (<1 kDa) size fractions for the field moist soil samples, but with differences for large and small size fractions from the air-dried soil samples (Tables 2, 3). The C/N ratio of WSOM in the field moist soil samples was 9:1 for the agricultural soils for the large-size particles, increasing to about 12:1 for the small-size particles, but the ratio increased from

TABLE 3. Size Distribution of WSOC and WSON in the Field Moist Soil Samples From CRP, Forest, and Agricultural Land Uses

	WSOC, mg kg^{-1} of dry soil				WSON, mg kg^{-1} of dry soil				C/N Ratio		
Land Use	L	M	S	Impact	L	M	S	Impact	L	M	S
CRP	24.58	55.09	374.15	L ~ M < S	2.26	5.49	5.13	L < M ~ S	10.9	10.03	72.93
Forest	17.56	59.69	311.02	L ~ M < S	1.80	3.25	1.27	L ~ M ~ S	9.73	18.38	245.19
Agricultural	27.15	113.16	305.87	L < M ~ S	1.05	6.30	3.11	L < M ~ S	25.91	17.96	98.25
P (F test)	0.16	0.22	0.49		0.04	0.13	0.03				
LSD (0.05)	NS	NS	NS		0.92	NS	2.85				

Values are means of nine replicates. Statistical analysis was applied to WSOC and WSON among different land uses within each size fraction. For size comparison within the same land use: ~, statistically not significant at $P = 0.05$; > or <, significantly higher or lower with LSD ($N = 9$, $P \leq 0.05$). Significance test was not applied to C/N ratios.

L, large-size fractions (>0.45 μm); M, medium-size fractions (1 Da–0.45 μm); NS, not significant at $P = 0.05$; S, small-size fractions (<1 kDa).

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approximately 8:1 to 35:1 for CRP and from 12:1 to 75:1 for forest soil samples as the size became smaller (Table 2), indicating that small-size particles of WSOM in CRP or forest soils were less rich in N compared with that in arable soil. In contrast, the C/N of SWOM in air-dried soil samples changed from large- to the medium-size fraction but increased dramatically in the small-size fraction for all three land uses (Table 3). For the field moist soils, most WSOC and WSON were distributed in high- and small-size particles; whereas for air-dried soil samples, most WSOC was distributed in small-size fraction and WSON was less changed among size fractions. The C/N ratio of WSOM from the field moist soil samples was wider when molecule sizes decreased in CRP and forest soils, whereas the C/N ratio of WSOM in agricultural soil changed little. In contrast, in the air-dried soil samples, the C/N ratio increased prominently in the small-size fraction. Air-drying did not decrease the large-size particle fraction of WSOC for all land uses but did significantly increase medium- and small-size fractions of WSOC for all land uses (Table 4). In addition, air-drying decreased WSON in large-size fractions but increased it in the medium-size fractions for all land uses (Table 4). Only in the agricultural land use was the small-size fraction of WSON decreased by air-drying.

There are limited studies in which size distribution of WSOC and WSON from terrestrial ecosystems has been investigated (Delprat et al., 1997; Smolander and Kitunen, 2002; Kiikkilä et al., 2006). However, this study differs from those in two aspects: size fractionation and sampling layers. Sizes fractions were less than 1 kDa, 1 to 10 kDa, 10 to 100 kDa, and more than 100 kDa in the studies by Smolander and Kitunen (2002), Kiikkilä et al. (2006), and Delprat et al. (1997). In contrast, in this study, size fractions were less than 2.5 μm but more than 0.45 μm, 1 kDa to 0.45 μm, and less than 1 kDa. In fractionation of soluble organic matter in freshwater or ocean water, dissolved organic matter refers to the organic matter less than 0.45 μm and particulate organic matter is more than 0.45 μm (Amon and Benner, 1996; Smolander and Kitunen, 2002; Volkman and Tanoue, 2002; Kiikkilä et al. 2006). In most publications, DOC less than 1 kDa is considered to be small-size particles. Dissolved organic C (<0.45 μm) can be produced from mineralization of particulate organic matter or from desorption of DOC on mineral surfaces. Amon and Benner (1996) demonstrated that small-size DOC (<1 kDa) from fresh stream water is more resistant to decomposition than the large-size DOC (1–30 kDa). They concluded that large molecular sizes of DOC usually are more reactive. Zhang et al. (2011) reported that small-size WSOM migrates to lower soil profiles, suggesting that small-size WSOM may be more resistant to decomposition. However, in fractionation of soil-extractable organic C, Kiikkilä et al. (2006) found that both large (>100 kDa)- and small-size (<1 kDa) fractions were most biodegradable. In addition, the other major difference of this study from those previously published is different sampling layers. Smolander and Kitunen (2002) and Kiikkilä et al. (2006) sampled organic layers of forest soils in contrast to the mineral soil from three land uses (i.e., CRP, forest, and agriculture) in this study. In general, in forest floor organic layers, WSOM may reflect the compositions of fresh or partly decomposed plant residues, whereas WSOM in mineral soil layers may include soluble humus and semidecomposed or well-decomposed organic matter. Therefore, direct comparison of our research with the previous reports would be nearly impossible. But the results of this study set a benchmark for size dynamics of WSOM among different land uses.

Our study demonstrated that size distribution of WSOC and WSON was affected by land use. Forest soils and CRP contained a relatively large proportion of large molecules, whereas agricultural soils consisted of primarily small molecules. There are two ways that forest floor organic matter reaches deeper soil mineral layers: through leaching or through mixing by large soil fauna (i.e., bioturbation). Kaiser et al. (2002) reported a significant amount of high-molecular-weight fractions in pine and beech forest floor in autumn. Because there is lack of bioturbation caused by large soil fauna in the forest soil in subarctic area in this study (Zhang et al., 2012), the organic matter in forest mineral soil could result mostly from the downward movement of dissolved organic matter in the forest floor. This leached dissolved organic matter may contain large molecules (aromatic and aliphatic). Agricultural soils mostly have small molecules because of frequent disruption of tillage, enhanced decomposition, and N fertilization (Delprat et al., 1997).

As discussed earlier, air-drying increased total WSOC concentration and had a limited impact on WSON (Table 1). The gain in WSOC mostly occurred in the medium and small fractions, indicating that the increased WSOC could largely result from lysis of dead microorganisms in the drying process because 0.45-μm filter can remove most of the microorganisms in solution for field moist soil samples. Similarly, the air-drying process decreased WSON in large-size fractions but increased in medium-size fractions. In the large-size fractions, the agricultural soil samples had a smallest delta C/N ratio of 2.9 between fresh and air-dried soils, in contrast to the largest C/N ratio of 12.3 from the forest soil sample, with the C/N ratio of 7.3 of CRP sample.

TABLE 4. Differences of WSOC and WSON Between the Field Moist and Air-Dried Soil Samples for All Size Fractions and Land Uses

		WSOC, mg kg^{-1} soil					WSON, mg kg^{-1} soil					
Size Fraction	Land Uses	Field Moist	Air-Dried	Difference (Δ)	t	P	Field Moist	Air-Dried	Difference (Δ)	t	P	ΔC/N Ratio
>0.45 μm	CRP	68.94	24.58	44.36	1.64	0.12	8.36	2.26	6.10	2.31	0.03	7.3
	Forest	88.71	17.56	71.15	1.95	0.07	7.59	1.80	5.79	2.00	0.06	12.3
	Agricultural	36.41	27.15	9.26	1.09	0.29	4.26	1.05	3.21	3.26	<0.01	2.9
1 kDa–0.45 μm	CRP	10.06	55.09	−45.03	−2.05	0.05	0.52	5.49	−5.03	−4.89	<0.01	9.0
	Forest	8.26	59.69	−51.42	−2.92	0.01	0.35	3.25	−2.90	−2.38	0.03	17.7
	Agricultural	7.20	113.16	−105.92	−3.12	0.01	1.12	6.30	−5.18	−4.92	<0.01	20.4
<1 kDa	CRP	107.36	374.15	−266.79	−4.74	<0.01	3.02	5.13	−2.11	−1.37	0.19	126.4
	Forest	146.95	311.02	−164.07	−4.20	<0.01	1.94	1.27	0.67	0.88	0.39	244.9
	Agricultural	118.90	305.87	−186.97	−3.96	<0.01	9.94	3.11	6.83	2.69	0.02	27.4

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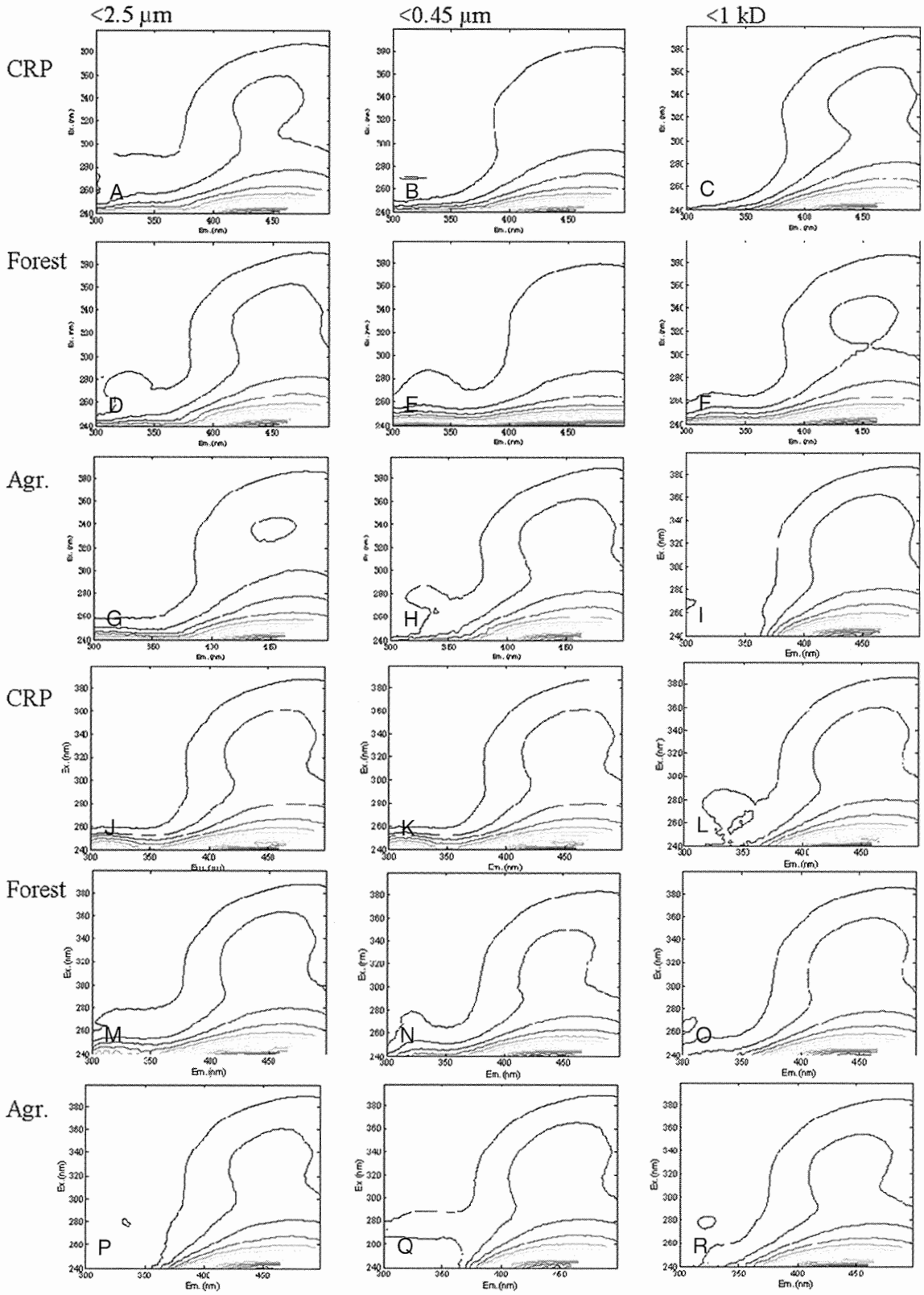

FIG. 1. Fluorescence excitation-emission matrix of WSOM from fresh CRP (A, <2.5 um; B, <0.45 um; C, <1 kDa), fresh forest (D, <2.5 um; E, <0.45 um; F, <1 kDa), fresh agricultural soil (G, <2.5 um; H, <0.45 um; I, <1 kDa), air-dried CRP (J, <2.5 um; K, <0.45 um; L, <1 kDa), air-dried forest (M, <2.5 um; N, <0.45 um; O, <1 kDa), and air-dried agricultural soil (P, <2.5 um; Q, <0.45 um; R, <1 kDa). Ex, excitation wavelength (in nanometers); Em, emission wavelength (in nanometers). Fluorescence intensities are in Raman units (RU).

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These data could reflect differences in microbial populations caused by varying land use, that is, bacteria (narrow C/N ratio) predominate in the agricultural soils, fungi (wide C/N ratio) in the forest soils, and a combination of bacteria and fungi in the CRP soils. Comparing the C/N ratios among the three size fractions, the C/N ratio increased as size fraction decreased. The C/N ratio in large-size fractions resulted from the fact that the loss of WSOC and WSON concentration in air-drying process was smaller than the C/N ratio of the medium- and small-size fractions resulting from gain of WSOC and WSON in air-drying, indicating that some of the WSON became insoluble during the air-drying process.

Fluorescence Compositions of WSOM

Representative contour plots of WSOM are shown for different size fractions and land uses in Fig. 1. Samples from different size fractions and land had similar broad peaks at Em 450 nm/Ex 240 nm and Em 450 nm/Ex 330 nm. We used PARAFAC analysis for all samples to further detect the possible functional pools of WSOM. Three fluorophore components decomposed by PARAFAC analysis were found for all difference size fractions and land uses: (i) a typical terrestrial humic substance-like fluorophore (Em 474–480 nm/Ex 240 and 348 nm); (ii) a marine or freshwater humic-like component; and (iii) a tyrosine-like component (Fig. 2). The spectral peak of Component 1 has been widely reported as a typical terrestrial humic substance-like fluorophore (Em 474–480 nm/Ex 240 and 348 nm) (Chen et al., 2003; Fellman et al., 2008; Ohno and He, 2011). This component is considered to be highly conjugated and more aromatic (Coble, 1996). Component 2 also had two excitation wavelengths (Ex 240 and 312 nm) and a single emission peak (Em 405–408 nm). This latter peak is attributed

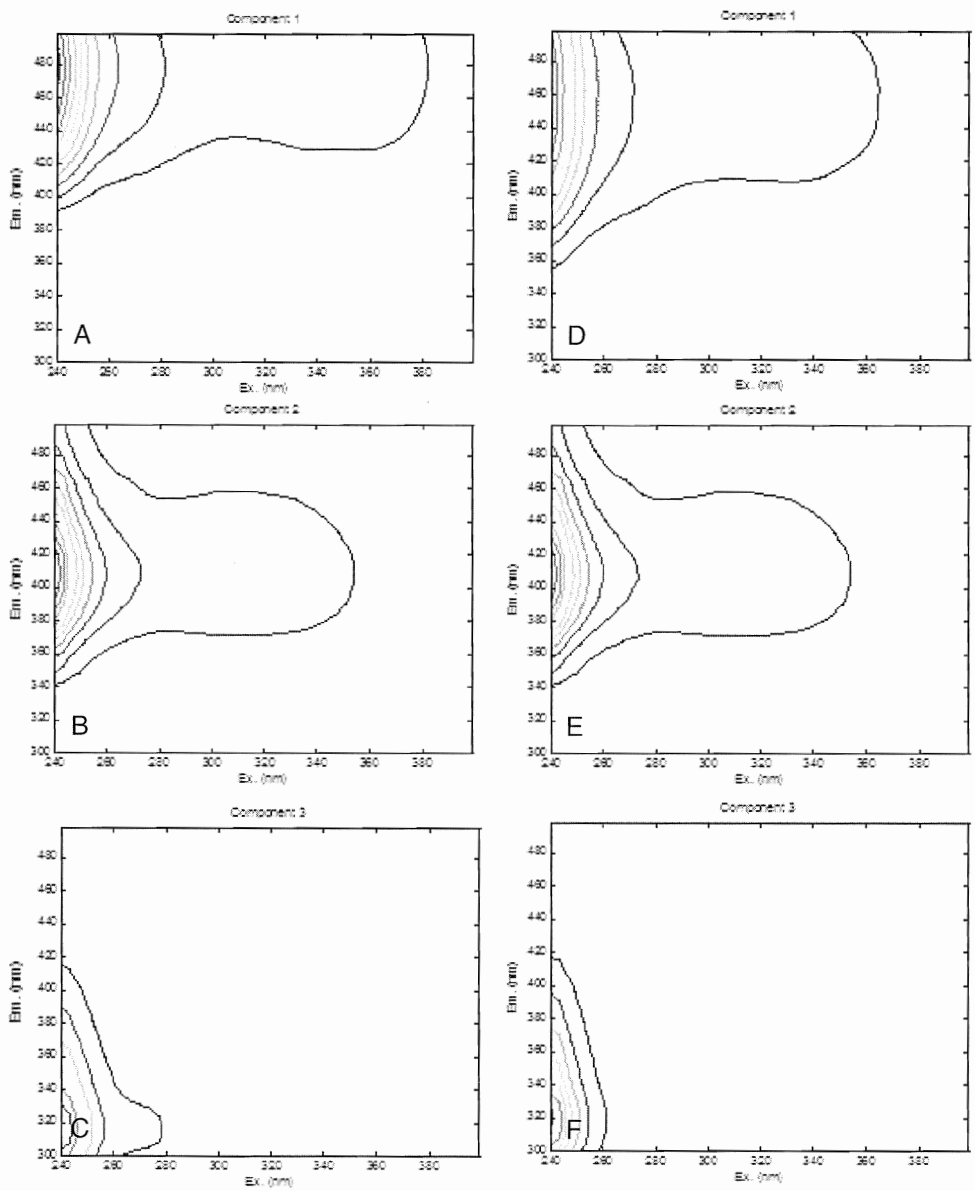

FIG. 2. Fluorescence components of WSOM for fresh soil (A, component 1; B, component 2; C, component 3) and air-dried soil (D, component 1; E, component 2; F, component 3). Ex, excitation wavelength (in nanometers); Em, emission wavelength (in nanometers). Fluorescence intensities are in Raman units (RU).

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to the marine or freshwater humic-like component (Yamashita and Tanoue, 2004; Stedmon and Markager, 2005; Fellman et al., 2008). The pattern of this component is also similar to the component observed from the water extracts of soil, plant biomass, and animal manure (Ohno et al, 2009; Ohno and He 2011). Component 3 showed strong emission in the 312- to 315-nm range at the low excitation wavelength of 240 nm, which is assigned to tyrosine-like components (Coble, 1996; Chen et al., 2003).

Previous studies have reported that fluorescence properties of dissolved soil organic matter is decomposed into components, such as humic-like, fulvic-like, trypotophane-like, and tyrosine-like materials. Ohno and Bro (2006) used water extraction of a variety of organic materials (soil, wetland plants, manures, tree leaves, and crop) and reported five components, which has the same number of components reported by Ohno et al. (2009) in water- and NaOH-extracted and XAD-8–separated humic and fulvic acid. Ohno and Bro (2006) suggested that a great number of samples and more organic matter sources are needed to determine the number of fluorophores in a solution. In seawater and freshwater studies, more fluorescence components (e.g., tyrosine-like, tryptophane-like, marine humic-like, and humic-like) are reported because of input of terrestrial organic matter and organic matter released from marine organisms such as phytoplankton (Yamashita and Tanoue, 2004; Stedmon and Markager, 2005). In a study of dissolved organic matter in wetland soils, nine fluorescence components, including various humic-like, fulvic-like, tyrosine-like, and tryptophane-like substances, were found because of input of various organic sources from groundwater, surface runoff, and upland (Fellman et al., 2008). In our study, soils were sampled from CRP, agricultural, and forest mineral surface. The source of organic matter was all from plant- or microorganism-derived soluble organic matter in soils. That perhaps is the reason why there are less fluorescence components in our study as compared with those of previously reported studies. In general, soil WSOM has a strong self-similarity in fluorescence property (Ohno and Bro, 2006).

Studies on fluorescence composition in molecular size fractions have been conducted mostly with seawater. In surface seawater, all molecular size fractions contain components of tyrosine-like, tryptophan-like, marine humic-like, and humic-like fluorophores (Yamashita and Tanoue, 2004). In contrast, WSOM in this study was from soils of different land uses, and yet all size fractions consisted of similar components: humic-like and tyrosine-like substances. However, no tryptophan-like component was found. Tryptophan-like component indicates the presence of intact proteins or less degraded peptide material, whereas the tyrosine-like fluorescence may be more degraded peptide material (Mayer et al., 1999; Yamashita and Tanoue, 2004; Fellman et al., 2008). Hence, existence of tyrosine-like substanes but not tryptophan-like in WSOM in this study is evidence that WSOM from mineral soils was dominated by decomposed protein rather than relatively large intact protein or peptides.

Relative Loadings of Fluorescence Compositions in WSOM

Most of the fluorescence of WSOM was in terrestrial humic-like (>50%) and marine/freshwater humic-like components (between 24% and 40%) (Fig. 3A, B, D, E). Only a small portion (all but one <25%) was in tyrosine-like component (Fig. 3C, F). This is apparently consistent with the amount of WSOM extracted from soil (Table 1) and agrees with literature reports (Yamashita and Tanoue, 2004; Ohno and Bro, 2006). Jones and Willett (2006) reported that the air-drying process increases total WSOC and WSON. However, this research showed that humic-like fractions increased whereas the protein-like component decreased. Although the results of relative loading cannot be used for direct comparison with the results from Jones and Willett (2006), which is in absolute concentration, the relative loading results of this study lead to the further understanding of the effect of drying on WSOM for each component.

For all three components, there were no statistical differences ($P > 0.05$) for each size fraction among land uses (Fig. 3) except for the terrestrial- and marine humic-like components of less than 1-kDa fraction. For the same component of each land use, the relative loadings of terrestrial humic-like component for the field moist soil sample extraction was not different ($P > 0.05$) among the three size fractions for each of the land uses (Fig. 3A). For the air-dried soil samples, this component increased in the forest ($P < 0.05$) and the agriculture samples ($P < 0.05$) but not for CRP ($P = 0.07$) as size fractions decreased (Fig. 3D). Compared with the relative loading of field moist with air-dried soil samples for each land use and each size fraction for the terrestrial humic-like component, the t test indicated some changes for this component (five were significant ($P < 0.05$) and four were not ($P > 0.05$)). The relative loading of marine/freshwater humic-like component increased as size fractions decreased for the forest ($P < 0.05$) and the agricultural ($P < 0.05$) land uses but not for CRP for both field moist and air-dried soil samples (Fig. 3B, E). Compared with the field moist and the air-dried soil samples, air-drying increased this component in each land use and size fraction ($P < 0.01$). These data support the conclusion that part of the WSOM increase in air-dried soils was caused by the humic materials of these soils, as proposed by Haynes (2000). The relative loadings of the tyrosine-like component in all land uses were reduced as molecule sizes decreased especially for WSOM from air-dried soil. There were statistical differences ($P < 0.05$) for the CRP, forest, and agricultural land uses among different size fractions for WSOM from air-dried soil samples, but such difference was only found in the forest soil in WSOM from the fresh soil sample ($P < 0.01$) (Fig. 3C, D). The t test showed that air-dried process significantly ($P < 0.01$) decreased the tyrosine-like component in WSOM of all three size fractions.

Fluorescence HIX of WSOM

Compared among the land uses, no difference ($P > 0.05$) in the field moist soil samples for HIX was found (Fig. 4C). Similarly, no difference ($P > 0.05$) was found among land uses for HIX in the air-dried soil samples (Fig. 4F). However, the HIX was higher ($P < 0.05$) in the size fractions less than 0.45 μm and less than 1 kDa than in the size fraction less than 2.5 μm for the forest soil but not for the CRP and agricultural land uses (Fig. 4C). In contrast, higher ($P < 0.05$) HIX in less than 2.5 μm than less than 1 kDa fraction was found in the agricultural but not the forest and CRP soils for the air-dried samples (Fig. 4F). Humification Index of WSOM is a ratio of fluorescence intensity of high quartile (sum of fluorescence intensity from 435 to 480 nm, high-humified compounds) over low quartile (sum of fluorescence intensity from 300 to 345 nm, low-humified compounds). High-quartile fluorescence intensity indicates existence of condensed (i.e., low H/C ratio) organic matter in solution in contrast to less condensed (i.e., high H/C ratio) organic matter reflected by low-quartile fluorescence intensity (Zsolnay et al., 1999). Sequential filtration was used in this study. In sequential filtration, the less than 2.5-μm size fraction includes less than 0.45-μm and less than 1-kDa size fractions; similarly, the less than 0.45-μm size fraction also included the less than 1-kDa

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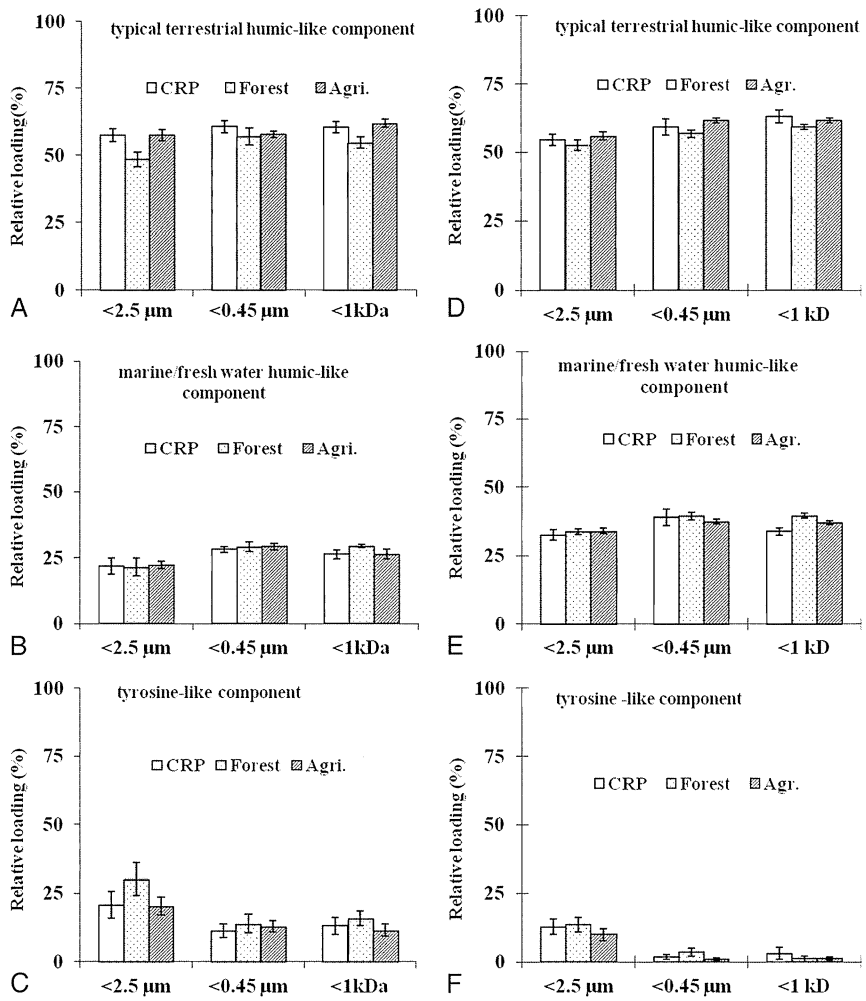

FIG. 3. Relative fractional loadings of PARAFAC components of WSOM under different land use and different size fractions from field moist soil samples (A–C) and air-dried soil samples (D–F). A, D, Typical terrestrial humic-like component; B, E, Marine/freshwater humic-like component; C, F, Tyrosine-like component. Vertical bars denote SE for nine replicates. Land uses: CRP, Conservation Reserved Program; Forest, land under forest; Agri, agriculture.

size fraction. Because of this, if fluorophores are in the large size fraction (<2.5 μm), the fluorescence intensity should decrease as the molecular size becomes smaller because of exclusion of large-size molecules by filtration. On the other hand, if fluorophores are in the small-size fraction (<1 kDa), the fluorescence intensity should be similar among all size fractions. This logic is based on no interactions among fluorophores of different size fractions or among organic matter molecules in different sizes, which can result in either fluorescence generation or cancellation. As illustrated in Fig. 4A, the low-quartile fluorescence intensity from CRP land of the field moist soils was consistent for all size fractions, indicating that the low-quartile fluorophores may exist in the small molecular size fraction (<1 kDa), and there was little interaction among three size fractions. Similarly, for the field moist soils of the agricultural and forest soils, fluorophores may also exist in the large (<2.5 μm)- and the small-size (<1 kDa) particles because there was a decrease from less than 2.5 μm to less than 0.45 μm and then an increase from 0.45 μm (Fig. 4A). The decrease indicated exclusion of the large-size fraction when filter was changed to less than 0.45 μm. The increase indicated that there was an interaction between less than 0.45-μm and less than 1-kDa size particles (Because of the sequential extraction, the fluorescence intensity of low quartile should be similar between <0.45 and <1 kDa if there was no interaction). For the high quartile, no difference ($P > 0.05$) was found for land uses for both field moist and air-dried soil samples. Compared among different size fractions, high quartile for less than 1 kDa was higher ($P < 0.05$) than that of less than 2.5 μm for all three land uses in the field moist soil samples (Fig. 4B). In the air-dried soil samples, the fluorescence intensity of high quartile was increased ($P < 0.05$ for CRP, but $P > 0.05$ for the forest and agricultural soils) from less than 2.5 μm to less than 0.45 μm, then decreased ($P < 0.05$ for all land uses) from 0.45 μm to less than 1 kDa (Fig. 4E). These changes again suggested an interaction of fluorophores between the adjacent size fractions. The HIX is the ratio of fluorescence intensity of high quartile (emission wavelengths of 450–480 nm) over the fluorescence intensity of low quartile (emission wavelengths of 300–345 nm). If there are interactions among different size molecules in WSOM in generation or cancellation of fluorescence, the HIX may not truly reflect the degree of humification of WSOM. Comparing the field moist and air-dried soil samples, there was no discernible trend (mix of

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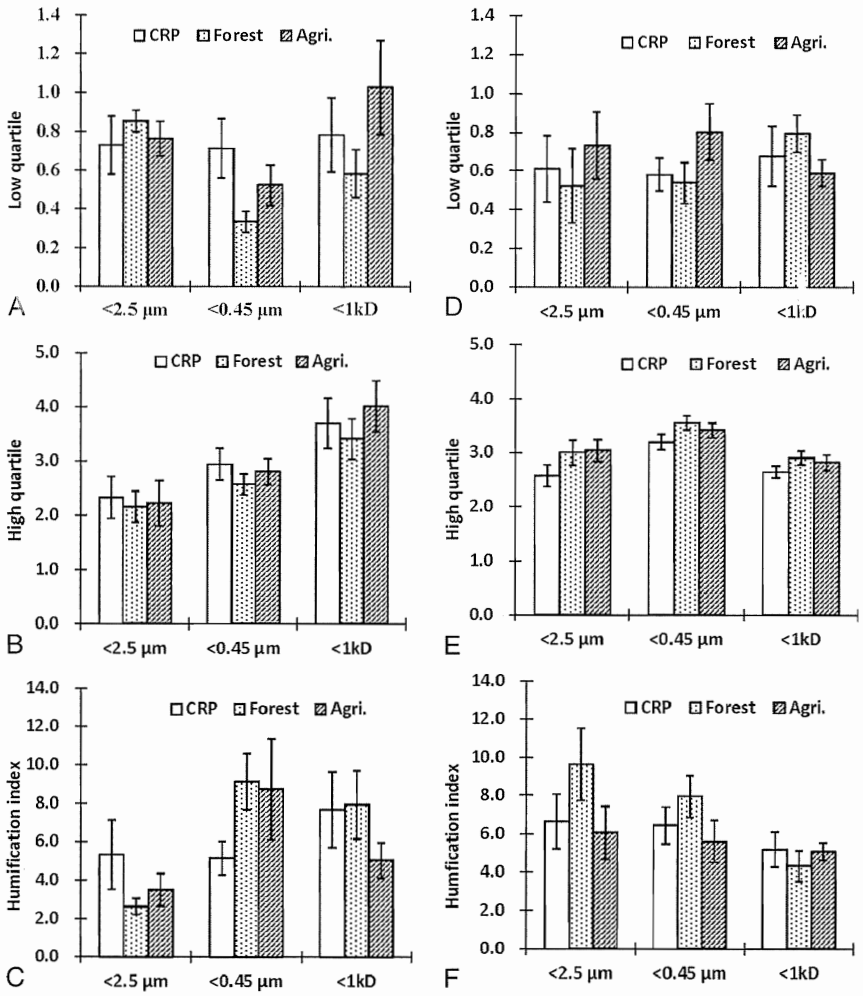

FIG. 4. Low-quartile, high-quartile, and Humification Index of WSOM of field moist (A–C) and air-dried (E–G) soil samples of land uses of agriculture, forestry, and CRP land.

increase or decrease for low quartile, high quartile, or HIX) for the impact of air-drying process.

CONCLUSIONS

In this study, we quantified and compared soil WSOC and WSON of field moist and air-dried soil samples under forest, agricultural, and grassland (converted from agricultural land for a CRP) managements in subarctic Alaska. Our data indicate that air-drying process increased WSOC for all three land uses. Size fractionation revealed that air-drying process also caused more WSOC distributed in the small size (<1 kDa) fraction. Thus, our results support the proposal that field moist soil samples are more suitable for characterizing the impact of soil management practices on soil WSOM.

With field moist soil samples, we observed the impact of land uses on WSOC but not WSON of soil in this high-latitude area. The WSOC contents decreased in the order: forest land > converted and conserved grassland > agricultural land. This order implies that the long-term agricultural land use could lower the WSOM levels in soils, but the decreasing trend could be reversed by conversion of agricultural land to grassland under conservation.

Fluorescence spectroscopic analysis revealed the presence of two humic-like components and a tyrosine-like component in the WSOM of these soil samples. There were no differences in the relative abundance of the three fluorophore components between different land uses and size fractions, indicating that the impact of land uses was mainly on the quantity, rather than on the composition, of WSOM. Air-drying slightly increased a marine/freshwater humic-like component, implying that part of the increase of WSOM by air-drying was from the release of humic materials in these soils.

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