Geoderma 149 (2009) 116–123

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Fluorescence spectroscopy studies of humic substance fractions isolated from permanently frozen sediments of Yakutian coastal lowlands

L.T. Shirshova *, A.L. Kholodov, B.N. Zolotareva, L.A. Fominykh, A.M. Yermolayev

Institute of Physicochemical and Biological Problems in Soil Science, Russian Academy of Sciences, Pushchino, 142290, Russia

ARTICLE INFO

Article history:
Received 14 December 2007
Received in revised form 1 November 2008
Accepted 23 November 2008
Available online 21 December 2008

Keywords:
Permafrost
Sediment
Soil
Humic substances
NOM
Resin-alkali extraction procedure
Synchronous fluorescence spectra

ABSTRACT

Predictions of global warming render studies of organic matter stored in permanently frozen sediments of northernmost areas particularly topical. This paper offers results of fluorescence spectroscopy applied to the study of humic and/or humic-like fractions gained from polygenetic syncryogenic sediments in northern Yakutia in comparison with humic substances (HS) from recent soil and the Nordic (NOM) reference of aquatic natural organic matter. To isolate HS fractions from sediment and soil samples the method of sequential extraction with sulfonate resin (HS-S fraction), carboxylate resin (HS-C fraction) and 0.1 M NaOH (HS-A fraction) was used. The HS extracts were filtered through a 0.45 µm membrane filter, following which part of each HS fraction was broken down into humic acids (HA) and fulvic acids (FA). Synchronous fluorescence spectra were obtained on aqueous solutions of all specific HS fractions as well as HA and FA fractions isolated thereof and NOM. Variations in the main peak position and intensity seen on the synchronous fluorescence spectra of HS-S, HS-C and HS-A extracted from the same soil/sediment sample are apparently indicative of the distinct degree of humification of the isolated fractions. It was found that HA fractions, compared to FA fractions, show a more varied array of fluorescence observations which change depending on the source of HS. Consistent with fluorescence-produced characteristics for HS and HA fractions, sediment samples can be classified into two groups, one comprising Pleistocene sediments of the ice complex, the other sediments of the Holocene thickness and Pleistocene buried soil. The HS and HA of the first group manifest dominating peaks in the low- and intermediate-wavelength spectral regions, which is indicative of a relatively low degree of humification and certain similarity to NOM. The HS and HA fractions of the second group show a fluorescence signals set typical of recent soil, where the dominating peak of a particular fraction occurs in the long-wavelength region peculiar to a high degree of humification.
An examination of experimental data suggests essential bioclimatic fluctuations in the region over the period of the studied sediments formation.

1. Introduction

At the present time organic matter stored in permanently frozen sediments of northernmost areas is a subject of unfailing interest. The predicted global warming followed by the melting of the frozen sediments may have as a consequence a release of the stored organic matter and its involvement in the current biogeochemical cycle. This will primarily be true for humic substances (HS), the refractory fractions of the natural organic matter which occur in all terrestrial and aquatic environments and affect many processes in biosphere (Aiken et al., 1985; Stevenson, 1994; Hayes and Clapp, 2001; MacCarthy, 2001, and references therein). The last few decades have seen a steady stream of publications on the chemistry of HS of differing origins, while systematic studies of HS stored in cryosphere are still lacking. It is pertinent to mention here that there is much controversy among researchers over the molecular structure of HS. In accord with an early concept, HS are polydisperse macromolecules (Swift, 1999 and references therein). In the past two decades a view of HS as supermolecular associations/aggregates of relatively low molecular weight components held together by weak interactions has been gaining popularity (Sutton and Sposito, 2005, and references therein). It should be noted that a study of a labile and dynamic molecular system like that implies application of mild techniques of isolation and treatment of the material assayed (Osterberg et al., 1994; Shirshova and Ermolaeva, 2001). Enduring are classical ideas of HS as a system of compounds of distinct chemical maturity ranging from components of low degree of humification to ones of high degree of humification (Hayes et al., 1989; Orlov, 1990; Stevenson, 1994). The formation of the latter would be ascribed to an increase in the degree of aromatic polycondensation and content of conjugated structures as well as to a loss of aliphatic, carbohydrate and polypeptidic compounds (Barancikova et al., 1997; Olk et al., 2000; Provenzano et al., 2001; Milori et al., 2002; Mafra et al., 2007).

---

* Corresponding author. Tel.: +7 4967 73 38 45; fax: +7 4967 33 05 95.
E-mail address: shirshova@issp.serpukhov.su (L.T. Shirshova).

0016-7061/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.geoderma.2008.11.026

Table 1
Identification of samples examined

Sample No.	Sample Identity	Age[a] (kyr)	Sample origin
1.	CL	1–2	Cover layer of ice complex
2.	AL	5	Peaty sediments of alas lake
3.	IC3	12–15	Ice complex
4.	BS	30	Buried soil
5.	IC5	50	Ice complex
6.	IC6	200	Ice complex
7.	SH	Recent	Sodic haplustert, A hor.
8.	AS	Recent	Primitive cryogenic alluvial soil, A hor.
9.	BhC	Recent	Podzol, BhC hor.
10.	NOM		The Nordic (NOM) reference of aquatic natural organic matter

[a] By Schiermeister et al. (2002).

Table 2
HS yield obtained by resin–alkali extraction–fractionation technique

Sample No.	Sample Identity	Corg, (g kg^{-1})	HS yield, % Corg HS-S	HS-C	HS-A
1	CL	82.4 (1.1)[a]	0.85 (0.03)	1.64 (0.05)	27.85 (0.71)
2	AL	63.5 (0.4)	0.79 (0.02)	3.37 (0.10)	29.29 (2.64)
3	IC3	16.0 (0.8)	11.07 (0.33)	8.31 (0.25)	7.39 (0.29)
4	BS	33.6 (1.4)	10.33 (0.31)	9.23 (0.28)	12.53 (1.08)
5	IC5	14.9 (0.8)	12.8 (0.38)	6.00(0.18)	16.8 (1.51)
6	IC6	5.9 (0.4)	20.3 (0.61)	10.20 (0.31)	13.6 (1.22)
7	SH[b]	30.2 (0.4)	19.27 (0.58)	14.47 (0.43)	12.4 (1.12)
8	AS[b]	9.4 (0.8)	14.02 (0.42)	10.33 (0.31)	19.19 (1.73)
9	BhC	1.3 (0.8)	5.48 (0.18)	10.00 (0.40)	2.31 (0.04)
10[c]	Tundra[b]	17.0 (0.8)	7.12 (0.21)	12.43 (0.37)	18.81 (1.69)
11[c]	Soddy podzolic[b]	23.2 (1.3)	3.93 (0.12)	11.21 (0.34)	16.41 (1.48)

[a] Values in parentheses are standard deviations of three laboratory replications.
[b] Humic-accumulative horizon.
[c] Data were reported in Shirshova and Khomutova (1994) and used for comparison.

Identification and characterization of HS heavily relies on fluorescence spectroscopy remarkable for its instant response and minimum preparation requirements for the materials (MacCarthy and Rice, 1985; Bloom and Leenheer, 1989; Senesi et al., 1991; Belin et al., 1993; Frimmel, 2000; Chen et al., 2003). In conformity with the principles of fluorescence spectroscopy, an increase in the degree of conjugation of the humic aromatic/unsaturated systems goes along with a drop in fluorescence intensity and a shift of the fluorescence maximum into the long wavelength region (Ghosh and Schnitzer, 1980; Ewald et al., 1988; Miano et al., 1988; Senesi et al., 1991). This enables the fluorescence parameters to be used as a measure of the degree of humification, or — which is the same — of the chemical maturity of HS. There is a consensus that the fluorescence of the fulvic acids (FA) is mainly caused by relatively simple aromatic/phenolic compounds, whereas the fluorescence of the humic acids (HA) is due to extensively conjugated phenolics and quinoids (MacCarthy and Rice, 1985; Miano et al., 1988; Bloom and Leenheer, 1989; Senesi et al., 1991; Chen et al., 2003).

The methods used for the isolation of HS from their source have an important impact on their following analysis (Hayes, 1985; Hayes and Clapp, 2001). For instance it was clearly reported that the sequential resin–alkali extraction–fractionation technique (Shirshova, 1991; Shirshova et al., 2006a,b) offers advantages in characterizing soil HS as it allows milder isolation conditions compared to the classical procedure thereby preserving the native structure of HS (Shirshova and Yermolayev, 1990; Shirshova and Khomutova, 1994; Shirshova et al., 1999). In the present work we made use of the above mentioned extraction technique to isolate humic and/or humic-like fractions from permafrost sediments. The isolates were analyzed by fluorescent spectroscopy and compared to the aquatic natural organic matter and to HS that were obtained from the recent soil via the same extraction procedure (resin–alkali extraction–fractionation). Our results allowed us to determine specific structural features of permafrost HS and to provide an important insight into the degree of their chemical maturation.

2. Materials and methods

2.1. Samples

The investigation is concerned with permafrost aleurites syncryogenic sediments of different genesis and age collected from borehole

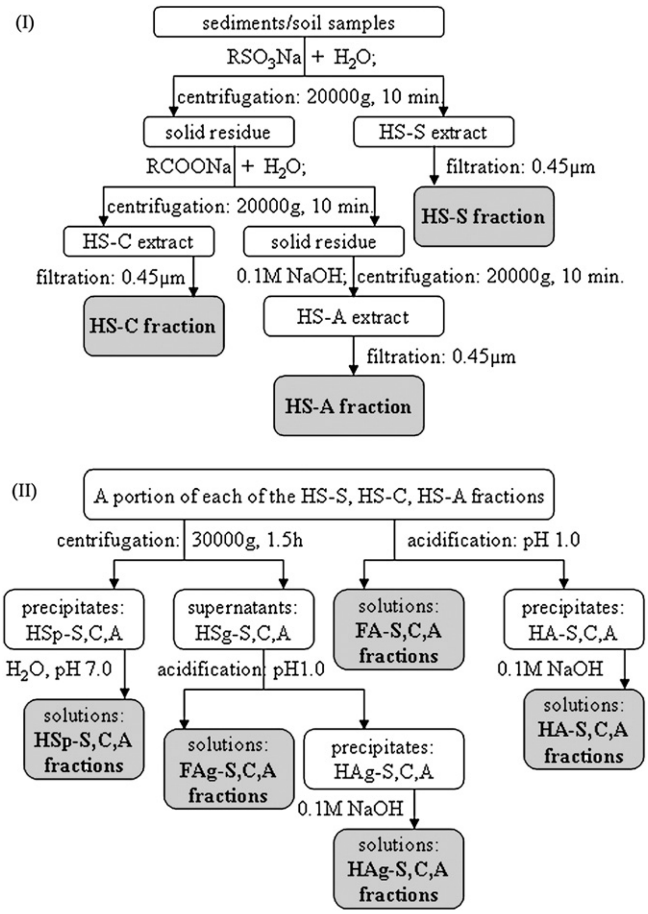

Fig. 1. Scheme of isolation of the humic fractions investigated: (I) the sequential resin–alkali extraction–fractionation procedure; (II) the procedure of isolation of fulvic acid, and humic acid fractions and HSp fractions.

Table 3
Wavelengths (λ_{max}) of the main synchronous spectral peaks for fulvic acid fractions, obtained with (FAg) and without (FA) centrifugation of initial humic substance fractions

Sample identity[a]	λ_{max} HM[b] FA-S / *FAg-S*	FA-C / *FAg-C*	FA-A / *FAg-A*
SH	338 (a)	339 (a)	369 (b)
	349 (a)	*369 (b)*	*371 (b)*
AS	336 (a)	332 (a)	332 (a)
	n.d.[c]	n.d.	n.d.
IC3	348 (a)	348 (a)	366 (a)
	338 (a)	*334 (a)*	*358 (a)*
BS	376 (b)	370 (b)	363 (a)
	376 (b)	*338 (a)*	*359 (a)*
BhC	346 (a)	333 (a)	333 (a)
	n.d.	n.d.	n.d.

[a] Abbreviations are described in footnotes of Fig. 1 and Table 1.
[b] Each data was average of three replicate measures (spectra replications were found to be identical within the limit of precision of our apparatus).
[c] n.d. — not determined.