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# Chemistry and spectroscopic properties of surface horizons of Arctic soils under different types of tundra vegetation - A case study from the Fuglebergsletta coastal plain (SW Spitsbergen)

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# ABSTRACT

Detailed studies of soil organic matter (SOM) are currently very important, especially in the permafrost-affected soils of the High Arctic, as many of these soils contain quite a large amount of SOM, which may be very susceptible to decomposition due to climate change. The main objective of this study was to determine the chemistry and spectroscopic properties of surface horizons (O, A, AC) of High Arctic soils under different types of tundra vegetation in the eastern part of the Fuglebergsletta coastal plain (Hornsund area, SW Spitsbergen) in the context of SOM susceptibility to decomposition due to climate change. The obtained results indicate that soils covered with wet moss and ornithocoprophilous tundra vegetation exhibits significantly higher carbon and nitrogen content in comparison with soils covered with lichen-heath, polygonal, and geophytic initial tundra vegetation. Despite differences in the elemental composition of all the soil surface horizons, the mean C/N ratio for the studied horizons is low and similar (i.e. from 9 to 14). This indicates that C/N ratio is not a good indicator of degree of organic matter decomposition for the High Arctic soils occurring in areas affected by seabirds. A high E<sub>4</sub>/E<sub>6</sub> ratio (i.e. ratio of UV–Vis absorbance measured at 472 nm and 664 nm and often called humification index) for NaOH-soluble humic substances indicates that the humic substances present in the studied surface horizons of soils covered with wet moss, ornithocoprophilous, and lichen-heath tundra vegetation are characterized by a low degree of humification. The Fourier transform infrared (FTIR) spectroscopy data indicate a prevalence of aromatic rings over aliphatic chains in the surface horizons of Cryosols under polygonal, geophytic initial, and lichen-heath tundra vegetation. Surface horizons of soils covered with wet moss and ornithocoprophilous tundra vegetation types exhibit a prevalence of aliphatic chains over aromatic rings. Such soils, which occupy about one third of the studied area, may act as carbon sources in the context of the emission of greenhouse gases into the atmosphere if the global air temperature will still rise. On the other hand, SOM from the surface horizons of soils covered with polygonal and geophytic initial tundra vegetation and occupying about 40% of the studied area, exhibits low potential susceptibility to decomposition.

#### 1. Introduction

Soil organic matter (SOM) is one of the most important constituents of the Earth's surface, because it plays a crucial role in many environmental reactions and processes such as the sorption of water, elements, and pollutants. In addition, SOM is an important source of nutrients (nitrogen, phosphorus) for plants and energy for microorganisms (Stevenson, 1994; Uhlířová et al., 2007). SOM affects soil formation and its chemical and physical properties such as pH, cation exchange capacity, color, and thermal properties (Baldock and Skjemstad, 2000; Stevenson, 1994). While SOM has been the subject of many studies for more than a century, there still remain many gaps in knowledge on SOM composition, formation, conversion, as well as decomposition (Schmidt et al., 2011; Sjögersten et al., 2003; Stevenson, 1994).

Detailed studies of SOM are currently very important, especially in the permafrost-affected soils of the High Arctic, as many of these soils contain a large quantity of SOM (Ernakovich et al., 2015; Hugelius et al., 2010, 2014; Kuhry et al., 2013; Sjögersten et al., 2003; Tarnocai et al., 2009; Uhlířová et al., 2007; Xu et al., 2009; Zubrzycki et al., 2013), which may be very susceptible to decomposition due to climate change. In addition, the decomposition of SOM may be responsible for positive feedback to climate warming due to the release of a large amount of greenhouse gases (CO2, CH4) into the atmosphere (Andersen and White, 2006; Kuhry et al., 2013; Moni et al., 2015; White et al., 2004; Zubrzycki et al., 2013). According to the literature, SOM susceptibility (or vulnerability) to decomposition varies strongly by

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geographic area, as it depends on the physical and chemical properties of SOM (chemical and molecular composition, structural complexity, degree of humification), soil thermal and moisture regimes as well as the quantity and quality of soil microbial communities (Aerts, 2006; Andersen and White, 2006; Dai et al., 2002; Ernakovich et al., 2015; Moni et al., 2015; Nadelhoffer et al., 1992; Schmidt et al., 2011; Uhlířová et al., 2007; Wei et al., 2014; White et al., 2004). In addition, soil pH, nutrient availability, stability of soil aggregates, soil texture, and soil mineral composition all play an important role in the susceptibility of SOM to decomposition by soil microbes (Baldock and Skjemstad, 2000; Balesdent et al., 2000; Kaiser and Guggenberger, 2003, 2007; Kalbitz et al., 2005; Kögel-Knabner et al., 2008; White et al., 2004; Xu et al., 2009).

Due to the marked complexity of the structural, molecular, and elemental composition of SOM, many different methods including Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), cross polarization magic-angle spinning nuclear magnetic resonance spectroscopy (13C CP-MAS NMR), molecular fluorescence spectroscopy (MF), and electron spin resonance spectroscopy (ESR) are very useful and often applied in SOM studies (Celi et al., 1997; Chen et al., 2002; Cocozza et al., 2003; Gressel et al., 1995; Heller et al., 2015; Inbar et al., 1989, 1990; Kalbitz et al., 1999; Lobartini and Tan, 1988; Niemeyer et al., 1992; Zbytniewski and Buszewski, 2005). However, such detailed chemical and spectroscopic studies of SOM from High Arctic soils are still very rare (Andersen and White, 2006; Dai et al., 2002; Dziadowiec et al., 1994; Ernakovich et al., 2015; Gentsch et al., 2015; Moni et al., 2015; Uhlířová et al., 2007; Xu et al., 2009). In addition, many of the abovementioned chemical and spectroscopic studies were conducted on different SOM fractions extracted from bulk soil samples by means of different physical and/or chemical protocols designed to simplify analysis. However, it is known that extraction procedures may slightly or even significantly alter the chemical composition, structure, and properties of extracted SOM (Bernier et al., 2013; Ernakovich et al., 2015; Heller et al., 2015; Kögel-Knabner, 2002; Sjögersten et al., 2003).

The detailed knowledge about quantity and quality of organic matter accumulated in soils of the High Arctic is extremely needed to improve future models concerning climate change caused by release of greenhouse gases ( $CO_2$ ,  $CH_4$ ) into the atmosphere due to the large dimensions of the High Arctic and often high content of SOM in the soils of that region.

Thus, the main objective of this study was to determine the elemental composition and spectroscopic properties of surface horizons of High Arctic soils covered with different types of tundra vegetation in the eastern part of the Fuglebergsletta coastal plain in the Hornsund area of SW Spitsbergen using elemental analysis (CHNS) as well as UV–Vis and FTIR spectroscopy in the context of SOM susceptibility to decomposition due to climate change. The elemental analysis (CHNS), UV–Vis and FTIR spectroscopy were used in this study, because the methods are: 1) complementary to each other, 2) not expensive, 3) require small amount of sample, 4) widely used in characterization of SOM, and 5) give detailed information about quantity and quality of SOM.

# 2. Materials and methods

# 2.1. Study area

Soil samples were collected from the eastern part of the Fuglebergsletta coastal plain, which is located between the Ariekammen-Fugleberget mountain chain and Hornsund (Fig. 1). The study area is characterized by a prevalence of metamorphic schist, paragneiss, quartzite, amphibolite, and marble (Czerny et al., 1993; Majka et al., 2010), which are usually mantled by coarse-grained marine deposits (Szerszeń, 1965; Szymański et al., 2013, 2015). The ice-core lateral moraine of the Hansbreen glacier occurs in the eastern

part of the study area. Haplic Cryosols, Hyperskeletic Cryosols, Reductaquic Cryosols, Turbic Cryosols, and Leptic Regosols Ornithic prevail in the area (Migała et al., 2014; Szymański et al., 2013, 2015). Vegetation is quite heterogeneous with wet moss tundra vegetation showing a prevalence of Sanionia uncinata, Warnstorfia sarmentosa, Straminergon stramineum, and Aulacomnium palustre occurring at wet sites with Reductaquic Cryosols (Fig. 2A); ornithocoprophilous tundra vegetation with Cerastium arcticum, Poa alpina, Salix polaris, Chrysosplenium tetrandrum, and Cochlearia groenlandica occurring on Leptic Regosols Ornithic at sites fertilized by seabirds (Fig. 2B); dry lichenheath (lichen prostrate) tundra vegetation showing a prevalence of Cetrariella delisei, Ochrolechia frigida, Salix polaris, Saxifraga oppositifolia, and Polytrichastrum alpinum occurring mainly on Haplic Cryosols (Fig. 2C); polygonal tundra with Dichotrix gypsophila, Anthelia juratzkana, and Nostoc spp. occurring on Turbic Cryosols (Fig. 2D); geophytic initial tundra vegetation featuring Saxifraga oppositifolia, Saxifraga cespitosa, Sanionia uncinata, and Nostoc spp. on the lateral moraine of the Hansbreen glacier with a prevalence of Hyperskeletic Cryosols (Fig. 2E and F) (Dubiel and Olech, 1992; Skrzypek et al., 2015; Wojtuń et al., 2013). More detailed information concerning soils and tundra vegetation types of the eastern part of the Fuglebergsletta may be found in Migała et al. (2014), Skrzypek et al. (2015), Szymański et al. (2013, 2015, 2016a, 2016b), and Wojtuń et al. (2013). The mean annual air temperature in the study area is -4.2 °C, total annual precipitation is 450 mm, and the mean annual temperature of the top one meter of the ground ranges between - 2.0 and - 3.0 °C (Marsz, 2013; Marsz and Styszyńska, 2007).

## 2.2. Field and laboratory methods

Soil samples (the uppermost 10 cm) from surface horizons (O, A, AC) were collected from sites differing in terms of soil type (Haplic Cryosols, Turbic Cryosols, Hyperskeletic Cryosols, Reductaquic Cryosols, Leptic Regosols Ornithic), tundra vegetation type (wet moss, ornithocoprophilous, lichen-heath, polygonal, geophytic initial), parent material of soil (marine deposits, glacial till, rocky debris), and wetness (dry, moist, wet) (Table 1, Fig. 2). Soil sampling was randomly performed in the course of field research studies on the determination of heterogeneity of soil cover of the eastern part of the Fuglebergsletta coastal plain (Szymański et al., 2013). Soil samples were collected in plastic bags and immediately air dried in the laboratory at room temperature. All samples were then gently crushed and sieved through a 2 mm sieve to separate coarse material (> 2 mm) from fine earth material (< 2 mm). All the laboratory analyses were done in fine earth material. Elemental composition of the soil surface horizons was determined by dry combustion using a CHNS elemental analyzer after homogenization of soil samples by grinding in a mortar. All the analyses were done in triplicate and then averaged. The ash content in the soil samples was determined by overnight combustion at 550 °C.

UV-Vis absorbance at 280 nm, 472 nm, and 664 nm was measured via a Specord 50 UV-Vis spectrometer (Analytik, Jena). For the purpose of these measurements, soil extracts were prepared according to the protocol given by Sapek and Sapek (1999). The steps taken were as follows: 1 g of soil sample was extracted with 50 ml of 0.5 M NaOH by shaking for 2 h using a rotational shaker and leaving overnight. Subsequently, the suspension was filtered using qualitative filters. The absorbance of 10 times diluted extract was then measured at 664 nm, absorbance of 50 times diluted extract was measured at 472 nm, and absorbance of 250 times diluted extract was measured at 280 nm. The same procedure was applied to deionized water extraction. The obtained absorbance values were used to calculate E<sub>280</sub>/E<sub>472</sub> (E<sub>2</sub>/E<sub>4</sub>),  $E_{280}/E_{664}$  ( $E_2/E_6$ ), and  $E_{472}/E_{664}$  ( $E_4/E_6$ ) ratios. The ratios were not calculated for AC horizons of Cryosols covered with polygonal, geophytic initial, and in some cases lichen-heath tundra vegetation, as the horizons contained a very small quantity of organic matter and could not be analyzed using UV-Vis spectroscopy.

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