

Content, Distribution, and Translocation of Trace Elements in Permafrost-Affected Environments of the Siberian Arctic

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Contents

Abstract

Permafrost-affected environments are characterized by slow biogeochemical cycles due to their low temperatures. The slow rates of biogeochemical processes in Arctic landscapes lead to a high susceptibility to contamination and to a low pollution resistance. Trace metals are one of the major groups of industrial pollutants and can reach the Arctic by different paths, namely through local human activity and via long-range atmospheric transport. At present, the knowledge about the background levels of trace metals and their behavior in soils of the Arctic Regions is very limited, and in particular research is needed to understand the effect of permafrost conditions on trace metal mobility and distribution. This question is particularly important in the light of anticipated changes of climatic conditions. The predicted temperature increase in the Arctic region may lead to an increase of the annual thaw depth of the soils and a change of the groundwater table, which may affect the spatial distribution of contaminants. Therefore, there is a special need to study the processes that govern trace metal distribution in soils affected by permafrost. This knowledge may also help to gain more information about the ecological state of Arctic ecosystems and to estimate possible effects from direct anthropogenic pollution and, subsequently, predicted climate change.

Northeast Siberia represents an area remote from evident anthropogenic trace metal sources. This fact affords an opportunity to investigate trace metal levels in pristine environments. Soil samples from the Lena River Delta region and its hinterland, collected in 2009, 2010, and 2011 were analysed. The element concentrations in studied soils varied greatly ranging, for example, from 0.01 to 0.71 mg kg⁻¹ for **Cd**, from 0.6 to 65.0 mg kg⁻¹ for **Cu**, from 0.9 to 55.4 mg kg⁻¹ for **Ni**, from 2.14 to 38.9 mg kg⁻¹ for **Pb**, and from 12.1 to 440 mg kg⁻¹ for **Zn**. It could be shown that the Lena River Delta and its hinterland are pristine and can serve as a reference region for determining human influences on permafrost-affected landscapes.

The obtained results showed that element properties and soil physical and chemical characteristics are one of the major factors controlling the element distribution in studied landscapes. Furthermore, topography features (e.g. micro-relief forms) and water drainage are likely to govern more intensive element migration to adjacent landscapes and their accumulation on natural physico-chemical barriers. This study also showed that the accumulation of trace elements by different vegetation types reflects mainly the plant's biogeochemical characteristics.

Abstract

Furthermore, the soil geochemical composition of natural tundra landscapes presumably controls the element uptake by plants.

A laboratory experiment was performed to determine how the temperature regime affects the contaminant distribution within the soil matrix at the boundary between a contaminated surface soil layer and an uncontaminated deeper soil layer. The hypothesis was that the water transfer to the freezing front will be accompanied by a downward migration of water soluble metals within the soil column. The results of this experiment showed that diffusion along the concentration gradient seemed to be the most important mechanism controlling the migration of water soluble forms of Cd and Pb in unsaturated soils. In the frozen soils, no clear relation between water migration and the metal distribution was found. A decrease of the Cd mobility in the lower parts of the frozen columns in comparison with the unfrozen columns, suggests that frozen soils acted as a temporal geochemical barrier restricting further downward Cd transport. However, the experimental data obtained is still not enough to understand all the mechanisms of transport processes that occur under natural conditions. To gain a better understanding of these mechanisms, further investigations are needed to provide explanations, which which allow to quantitatively asses element transport and could be introduced to existing analytical modelling methods.

The results of this research enable a better assessment of the ecological state of permafrost-affected soils as one of the major components of Arctic ecosystems in changing climatic conditions.

Zusammenfassung

Permafrostgeprägte Regionen sind durch langsame biogeochemische Stoffkreisläufe charakterisiert; dies ist durch das Niedrigtemperatur-Regime bedingt. Durch diese langsamen Stoffkreisläufe sind die arktischen Regionen sehr anfällig für Kontamination und haben eine geringe Toleranz gegenüber dem Eintrag von Schadstoffen. Spurenmetalle sind eine der größten Gruppen industrieller Schadstoffe. Sie können über verschiedene Wege in die Arktis gelangen, hauptsächlich durch lokale menschliche Aktivitäten und aus weiterentfernten Regionen durch atmosphärischen Transport. Informationen über Hintergrundgehalte von Spurenmetallen und ihre Rolle in arktischen Böden ist ergänzungsbedürftig, ins Besondere ist eine intensivere Untersuchung des Einflusses von Permafrost-Bedingungen auf Spurenmetall-Mobilität und –verbreitung notwendig. Diese Frage ist vor dem Hintergrund der prognostizierten klimatischen Veränderungen von Bedeutung. Der vorhergesagte Temperaturanstieg in der Arktis könnte zu einer Zunahme der jährlichen Auftautiefe in Permafrostböden und zu einer Veränderung der Bodenhydrologie führen. Solche Veränderungen können die räumliche Verteilung von eingetragenen Stoffen beeinflussen. Aus diesen Gründen ist es von besonderer Bedeutung, das die Prozesse, welche Spurenmetallverlagerung in Permafrostböden beeinflussen, genauer untersucht werden. Derartige Untersuchungen würden zudem mehr Informationen zur Situation des Ökosystems Arktis liefern und dazu beitragen, den Einfluss der vorhergesagten klimatischen Veränderungen auf die Mobilisierung anthropogener Schadstoffe besser zu verstehen.

Nordostsibirien stellt eine Region fernab nennenswerter anthropogen-bedingter Spurenmetalleinträge dar, und ist damit eine zur Untersuchung von Spurenmetall-Konzentrationen in naturbelassenen Landschaftsräumen hervorragend geeignete Region. Bodenproben aus dem Lena-Delta und dem Küstenhinterland aus den Jahren 2009, 2010 und 2011 wurden analysiert. Die Elementkonzentrationen in den untersuchten Böden zeigen eine große Varianz (z.B.: 0.01 bis 0.71 mg kg⁻¹ **Cd**, 0.60 bis 65.0 mg kg⁻¹ **Cu**, 0.90 bis 55.4 mg kg⁻¹ **Ni**, 2.14 to 38.9 mg kg⁻¹ **Pb**, und 12.1 bis 440 mg kg⁻¹ **Zn**). Es konnte gezeigt werden, dass das Lena-Delta und das Küstenhinterland naturbelassen und ohne nennenswerten anthropogenen Eintrag von Schadstoffen sind. Damit kann dieses Gebiet als ein Vergleichsstandort herangezogen werden, um den menschlichen Einfluss auf Permafrost-geprägte Regionen zu bestimmen.

Zusammenfassung

Die Ergebnisse zeigen, dass die Elementeigenschaften und die bodenphysikalischen und – chemischen Parameter die Hauptfaktoren bei der Element-Verbreitung in den untersuchten Landschaften sind. Darüber hinaus ist ein erheblicher Einfluss von Topographie und Hydrologie auf Elementverlagerungen in angrenzende Ökosysteme und auf Elementakkumulierung an physikalisch-chemischen Grenzflächen wahrscheinlich. Weiterhin zeigte diese Untersuchung, dass die Akkumulierung von Spurenelementen in verschiedenen Vegetationstypen die biogeochemischen Eigenschaften der Pflanzenarten widerspiegelt. Des Weiteren ist es wahrscheinlich, dass die geochemische Zusammensetzung naturbelassener Tundralandschaften die Elementaufnahme durch Pflanzen bestimmt.

Ein Laborexperiment wurde durchgeführt, um den Einfluss des Temperaturregimes auf die Schadstoffverteilung in der Bodenmatrix an der Grenzfläche zwischen kontaminierter Oberbodenschicht und nicht kontaminierter Unterbodenschicht zu beschreiben. Die aufgestellte Hypothese war, dass der Wassertransfer zur Frierfläche ("*freezing front*") von einer nach unten gerichteten Migration der wasserlöslichen Metalle in der Bodensäule begleitet werden würde. Die Ergebnisse zeigten, dass der wichtigste Transportmechanismus die Diffusion entlang des Konzentrationsunterschiedes zu sein schien, welcher die Migration von Cd und Pb in wasserungesättigten Böden bestimmt. In gefrorenen Böden konnte keine eindeutige Beziehung zwischen Wassermigration und Metallkonzentration festgestellt werden. Eine Reduktion der Cd-Mobilität in den unteren Bereichen der gefrorenen Säule, im Vergleich zu den ungefrorenen Bereichen, lässt vermuten, dass der gefrorene Boden als eine zeitweilig wirksame geochemische Barriere fungierte, welche eine weitere nach unten gerichtete Ausbreitung von Cd verhinderte. Die experimentell gewonnenen Daten sind jedoch nicht umfassend genug, um alle Mechanismen nachzuvollziehen, welche die Metallverlagerung in einer natürlichen Umgebung beeinflussen. Zum vertiefenden Verständnis sind weitere Untersuchungen notwendig, welche dann auch quantitative Vorhersagen als Beitrag zu existierenden analytischen Modellierungsmethoden ermöglichen könnten.

Die Ergebnisse dieser Studie erlauben eine verbesserte Bewertung der ökologischen Situation von permafrostgeprägten Böden, welche eine der wichtigsten Komponenten des arktischen Ökosystems in einem sich ändernden Klima darstellt.

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List of Symbols and Abbreviations

AAS	Atomic absorption spectrometry
a.s.l.	Above sea level
As	Arsenic
BC	Bioaccumulation coefficient
BS	Base saturation
CEC	Cation exchange capacity
Cd	Cadmium
Co	Cobalt
Cvg.	Coverage
Cu	Copper
DOC	Dissolved organic carbon
dw	Dry weight
EC	Electrical conductivity
EDA	Exploratory Data Analysis
Eh	Redox potential
Fe	Iron
GIS	Geographic Information System
h	Hour
Hg	Mercury
KA5	German key for soil classification (Bodenkundliche Kartieranleitung)
kg	Kilogram; $\text{kg} = 10^3 \text{ g}$
km	Kilometer
LOI	Loss on ignition
mg	Milligram; $1 \text{ mg} = 10^{-3} \text{ g}$
mL	Millilitre; $1 \text{ mL} = 10^{-3} \text{ L}$
Mn	Manganese
n.d.	Not determined
Ni	Nickel

List of Symbols and Abbreviations

OC	Organic carbon
OM	Organic matter
Pb	Lead
pH	Soil acidity
R _k	Element accumulation coefficient
Rpm	Rotation per minute
RSG	Reference Soil Group
QL	Quantification limit
SD	Standard deviation
TM	Trace metals
UNESCO	United Nations Educational, Scientific, and Cultural Organization
WRB	World Reference Base for Soil Resources
Zn	Zink

1. Introduction

Arctic ecosystems belong to the most sensitive regions of the world with regard to effects of human impact (Weller, 1995; Perel'man & Kasimov, 1999; Gulinska et al, 2003). The Arctic was once considered to be a pristine region. However, over the twentieth century worldwide emission of anthropogenic pollutants have increased and reached this remote area. Over this time, all natural media in the Arctic may have undergone perceptible changes caused by pollution which can reach this region mainly by long-range transport (Izrael, 1982; Presley, 1997).

Trace metals are one of the major groups of pollutants presented in industrial emissions. They can reach the Arctic by different paths, namely through local human activity and via long-range atmospheric transport (Ford et al, 1995; AMAP, 2005; Zhulidov et al, 2011). Local anthropogenic influence is represented mainly by mining activities which cause polyelemental emissions with a considerable amount of trace metals and metalloids. Examples for anthropogenic sources of trace metals in the Arctic are the Norilsk industry area in Western Siberia and mining industries in Kola Peninsula (Jaffe et al, 1995; Boyd et al, 1997; Kashulina, et al, 1997; Niskavaara et al, 1997; Reimann et al, 1997; Gregurek et al, 1998; Reimann et al, 1999; Opekunova et al, 2007; Boyd et al, 2009; Zhulidov et al, 2011). This locally defined human activity can lead to substantial pollution of arctic ecosystems across several hundred kilometres. The areas affected by these emissions develop into technogenic geochemical anomalies for a number of metals such as Ni and Cu. The input of trace metals to the Arctic region by long-range atmospheric transport has been demonstrated by many studies (Ottar, 1981; Barrie and Hoff, 1985; Barrie, 1986a; Barrie, 1986b; Maenhaut et al, 1989; Nriagu, 1989; Pacyna & Winchester, 1990; Barrie et al, 1992; Thomas et al, 1992; Akeredolu et al, 1994; Pacyna, 1995; Rovinskiy et al, 1995; Rahn et al, 1997; Durnford et al, 2010). Pollution that reaches the Arctic is observed as so-called “arctic haze”. Arctic haze occurs commonly during the winter season and results from strong south-to-north transport of a particulate matter. The transport is driven by the Siberian anticyclone which moves winter flow patterns from the Eurasian continent to the Arctic (Barrie & Barrie, 1990). The aerosol transport zone extends from northern Kazakhstan – southern Urals – Novosibirsk through the eastern Taymyr peninsula (Rahn et al, 1997). Further transport of aerosols occurs into the area over the Laptev Sea and the

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eastern Arctic Ocean where the aerosol diffuses and reaches the North American continent or major cyclonic regions in the Aleutians and southern Greenland (Barrie, 1992; Rahn et al, 1997). The main components of this particulate matter are sulfate, black carbon, As, Cd, Hg, Pb, Zn, and many other metals of anthropogenic origin (Barrie, 1996; Headley, 1996; Wadleigh, 1996). Nevertheless, the concentrations of most trace elements in arctic environmental components are generally lower than in sample media located in temperate zones.

Soil can function as a transport barrier by adsorbing contaminants and preventing their further migration to aquatic ecosystems for example through seepage water and groundwater (Dobrovolsky & Nikitin, 1986). Metals accumulated in soils are leached out slowly by the processes of erosion, weathering processes, and plant uptake (Kabata-Pendias & Pendias, 2001). Therefore, the period of metal half-removal from soils is much longer than in other environmental components. Permafrost soils are widespread in sub-Arctic and Arctic tundra. They are characterized by slow biogeochemical turnover rates, water saturation, reductive conditions, and the accumulation of organic matter (Tarnocai et al, 2009). Organic matter is capable of forming organo-mineral associations (Höfle et al, 2013) of the type that bind the majority of trace metals (Dube et al, 2001; Davranche et al, 2011) and therefore, can serve as a barrier for chemical pollutants. According to some authors (e.g. Moscovchenko, 2010), organic matter is one of the main factors controlling biogeochemical processes in Arctic landscapes, and is therefore, in charge of sustaining Arctic ecosystems.

The Arctic is a region where the global warming is predicted to be more evident than in temperate regions (IPCC, 2007). Warming in the Arctic can dramatically affect permafrost-affected areas causing changes in cryological conditions. Geothermal observations showed that temperature increase in rocks of western Yakutia – the typical example of a permafrost-affected area in the Russian Arctic – may influence the upper 60-80 m depth (Pavlov, 2008). As reported in some studies, climate change may also affect the contaminant pathways (Goryachkin et al, 1998; Gordeev, 2002; Hinzman et al, 2005; Macdonald et al, 2005; Liu et al, 2012; Stern et al, 2012). For example, changes in precipitation or in the balance between rain and snow in the Arctic can lead to enhanced airborne contaminant deposition (AMAP, 2005). Climate change and progressive anthropogenic impact may affect main soil properties such as carbon content and redox potential, leading to a modified migration ability of pollutants (Weller, 1995; Dube et al, 2001; Balbus et al, 2013). Particularly, the predicted increase of global warming will likely

intensify biogeochemical cycling within this large reservoir of carbon (Boike et al, 2012) including the bound trace elements in the upper layers of permafrost-affected soils. Considering the occurrence of local anthropogenic sources across the Arctic as well as long-range transport of pollutants to the polar region, there is the need to study the processes that govern trace metal distribution in soils affected by permafrost.

1.1 Scope of the present study

At present, northeast Siberia represents an area remote from evident anthropogenic trace metal sources. However, there is a risk of airborne pollution by trace metals from local anthropogenic sources connected to the settlements. One of the largest settlements in northeast Siberia is the town Tiksi (71° 42' 55.6" N, 128° 48' 46.3" E). The anthropogenic influence in Polar Regions is likely to increase with new industrial developments (Gautier et al, 2009; Dodin et al, 2010). The investigated area of northeast Siberia holds coal, oil, and gas deposits (Fig. 1) and faces the thread of fossil fuel exploration (Alekseev & Koz'min, 2005). With the socio-economic development associated with the establishment of fuel exploration industries there exists the potential risks of environmental pollution (Dodin et al, 2010). According to Alyabina et al (2008), soils in the north of middle and eastern Siberia are poorly drained and are characterized by high organic matter content and high values of cation exchange capacity and thus have a low potential self-purification capacity. The exploration of natural resources in this region together with a potential local impact may strongly affect soils and other environmental media and eventually lead to a degradation of tundra ecosystems. Therefore, it is important to establish baseline levels of trace metals of the investigated area as a basis for further environmental impact assessment of the Arctic region.

The trace metal distribution in water, marine and terrestrial sediments (Dai & Martin, 1995; Nolting et al, 1996; Rachold et al, 1996; Klassen, 1998; Alexander & Windom, 1999; Siegel et al, 2000; Hölemann et al, 2005; Cai et al, 2011), groundwater (e.g. Banks et al, 1995), air (e.g. Golubeva et al, 2013), vegetation (e.g. Wojtun et al, 2013) and fauna (Presley, 1997; Hargreaves et al, 2011; Routti et al, 2011; Dietz et al, 2013; Julshamn et al, 2013) of the Arctic regions has been studied in detail before. However, the presence and behavior of these substances in permafrost-affected soils remains poorly studied. A survey of current literature showed that

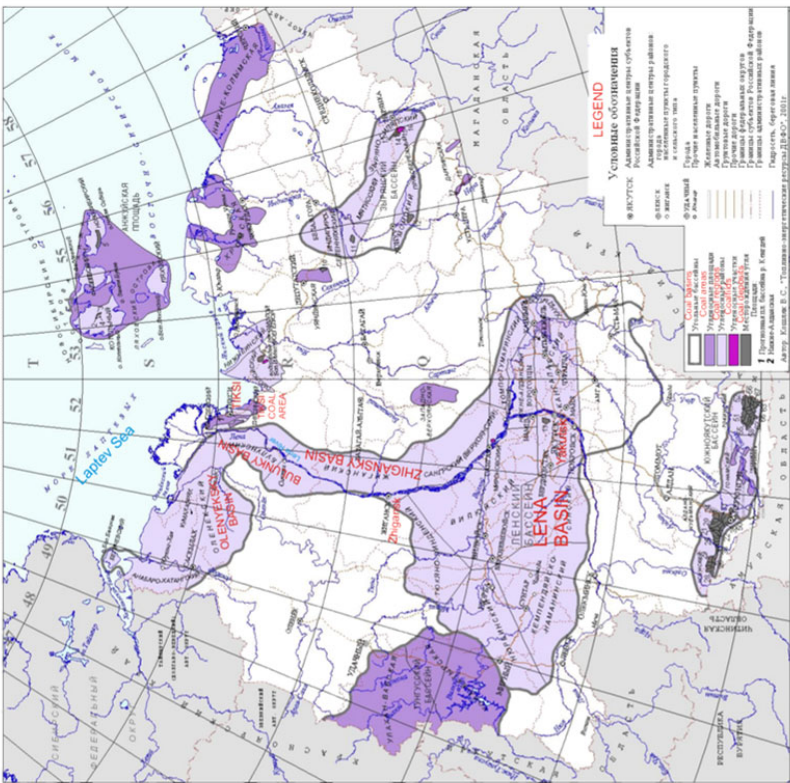
Chapter 1. Introduction

studies of trace metal content in permafrost-affected soils were concentrated on areas located in proximity to the sources of industrial emissions, coal mining, and oil and gas exploration. In Russia, these studies covered northeast European Russia (Walker et al, 2003, 2006a, 2006b, 2009) and western Siberia (Zhulidov et al, 1997b; Allen-Gil et al, 2003; Korobova et al, 2003; Moskovchenko, 2010; Zhulidov et al, 2011). Reviews of monitoring studies have been presented by Crock et al (1992) for the Alaskan Arctic. Much less of the published literature on soil chemistry relates to background trace metal concentration in Russian (Alekseeva-Popova, 1995; Rovinsky, 1995; Zhulidov et al, 1997a) and Canadian (Walker, 2012) Arctic soils. Crockett (1998) and Bargagli (2000) provided a study of background metal concentrations in the Antarctic region.

In the Arctic region, the river deltas are the most vulnerable areas of the terrestrial ecosystems since they may act as traps for chemical contaminants (Lisitzin, 1994). On the example of the Mackenzie Delta area it was shown that the chemical element transfer into permafrost-affected delta from the river catchments may be considerable (Dyke, 2001). The study of the element transport in permafrost-affected soils is important because hydrological and ecological changes due to climate warming and human activity in the Arctic region could increase element mobilization (Moskalenko, 1998; Serreze et al, 2000; Jorgenson et al, 2001; Hinzman et al, 2005; Schindler & Smol, 2006). Temperature increase may lead to permafrost zone degradation and, as a consequence, rising groundwater levels and enhanced export of DOC and other organic and inorganic substances to adjacent watersheds. This phenomenon causing more intensive thaw of deeper soil layers and change of ground water table may affect the vertical contaminant flux deeper into soil horizons as well. Cryoturbation processes which are common in arctic regions may also cause the contaminant transport to deeper soil horizons, as the input of these substances is taking place on the top soils.

FAR EASTERN FEDERAL DISTRICT
THE SAKHA (YAKUTIA) REPUBLIC
COAL-BEARING CAPACITY MAP
ДАЛЬНЕВОСТОЧНЫЙ ФЕДЕРАЛЬНЫЙ ОКРУГ
РЕСПУБЛИКА САХА (ЯКУТИЯ)
КАРТА РАЙОНИРОВАНИЯ УГЛЕНОСНОСТИ

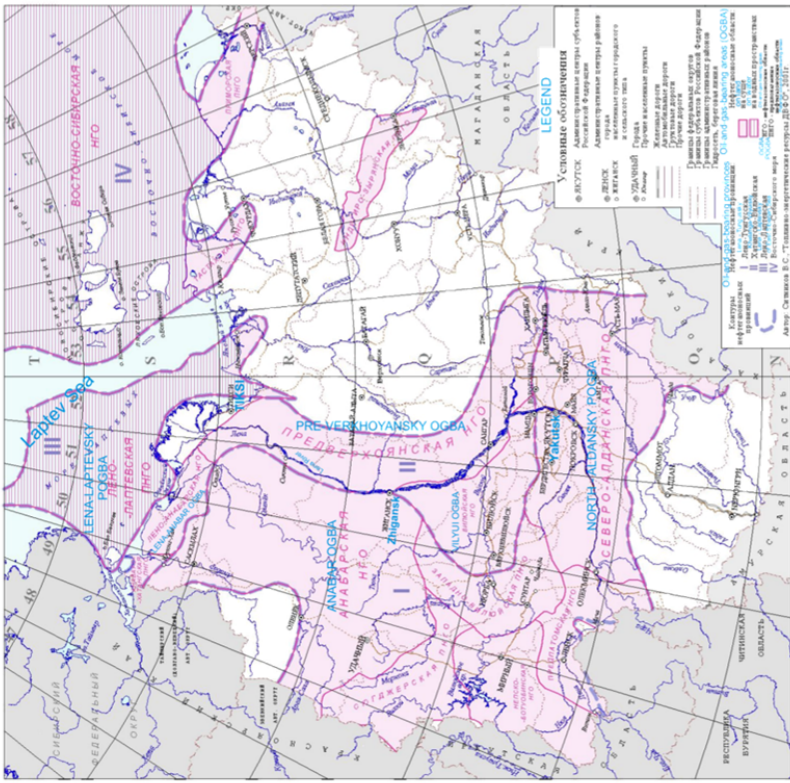
b



Koshlyak, Z. S., 2001

FAR EASTERN FEDERAL DISTRICT
THE SAKHA (YAKUTIA) REPUBLIC
OIL-AND-GAS-BEARING CAPACITY MAP
ДАЛЬНЕВОСТОЧНЫЙ ФЕДЕРАЛЬНЫЙ ОКРУГ
РЕСПУБЛИКА САХА (ЯКУТИЯ)
КАРТА РАЙОНИРОВАНИЯ НЕФТЕГАЗОНОСТИ

a



Sitnikov, V.S., 2001

Figure 1: Maps showing: (a) – oil-and-gas and (b) – coal bearing capacity of Sakha (Yakutia) republic including the area of the Lena River (Sitnikov, 2001; Koshlyak, 2001, slightly modified). Oil-and-gas bearing areas are pink-filled, the names of oil-and-gas bearing areas are blue-underlined, boundaries of coal bearing basins are shown as grey lines; coal bearing regions and areas are violet-filled, the names of basins are red-underlined.

1.2 Aims and objectives

The aim of this study was to provide the knowledge on the background levels of trace elements as well as on the landscape distribution of these elements in permafrost-affected soils of northeast Siberia in relation to soil properties. At the same time, experimental studies were required to understand the processes of the element transport in soils affected by frost.

The main objectives of this study were: (1) to provide the first soil geochemical data of the Lena River Delta region and its hinterland, (2) to investigate features of the spatial element distribution in representative landscape-geochemical units, (3) to reveal factors that affect the vertical element distribution in soils within the polygonal forms of the relief, (4) to detect hypothetical (local) anthropogenic sources in the study area contributing to the regional geochemical background, and (5) to determine how the temperature regime affects the trace metal behavior within the soil matrix by simulating the conditions on the boundary between the contaminated surface soil layer and a deeper uncontaminated soil layer.

The hypotheses of this study were: (1) The geochemical composition of the environmental components is affected by the geological aspects of the investigated area, (2) grain-size composition, organic matter, and in particular the temperature and hydrological regime are the major factors controlling the trace element distribution within the matrix of permafrost-affected soils, (3) the water transfer to the freezing front is accompanied by a downward migration of water soluble metals Cd and Pb within the soil column.

2. State-of-the-Art. Trace Metals and Permafrost-Affected soils

2.1 Trace elements in terrestrial ecosystems

2.1.1 Introduction

Until present in scientific literature the term “heavy metal” is often used in association with pollution and toxicity, although no consistent definition of this term exists. Several definitions of “heavy metals” are based on the density of the elemental form of the metal (e.g. [Morris, 1992](#); [Parker, 1994](#)), on atomic weight or mass (e.g. [Bennet, 1986](#); [Lewis, 1993](#); [Rand et al, 1995](#)), or on atomic number (e.g. [Lyman, 1995](#)). However, according to [Duffus \(2002\)](#) no relationship exists between density or any other foregoing physicochemical concepts and the toxicity or ecotoxicity applied to the term “heavy metal”. Some authors brought attention to the fact that this term comprises a wide array of elements which possess various chemical and biological properties (e.g. [Nieboer & Richardson, 1980](#)) and therefore, proposed a classification related to atomic properties and the solution chemistry of metal ions. In geochemical classification presented by [Ivanov \(1994-1997\)](#) the elements are divided into several groups in relation to the electronic structure of atoms. According to this classification the groups comprise elements of *s*- and *p*-sublevels (e.g. As, Ba, Ga, Pb), the transition elements of a *d*-sublevel (e.g. Cr, Cu, Zn), and so-called rare elements of *f*-sublevel (e.g. La, Pr, Y), where the type of a sublevel reflects the atomic reactivity of chemical elements.

The term “heavy metal” may alternatively be replaced with a term “trace metal”. This term comprises a diverse range of elements which depend on the kind of investigation. For example, from a geological point of view the group of trace metals includes the elements which occur in a diffused state although the concentrations of some of them in rocks differ significantly ([Alekseenko, 1990](#); [Il'yin, 1991](#)). In biological element classification, metals like Co, Cu, Mn, Ni and many others were considered as microelements ([Alekseev, 1987](#); [Davies, 1994](#)) because they are essential for living organisms. In fact, they may affect biota by occurring not only in high concentrations, but also in low concentrations, or due to disorder of the elemental ratio ([Motuzova, 2013](#)). In the current work the term “trace metal” is used to refer the group of the following elements considered as the most commonly encountered in soil chemistry studies and

Chapter 2. State-of-the-Art

those elements are often used for the assessment of anthropogenic influence on terrestrial ecosystems: *As, Cd, Co, Cu, Hg, Fe, Mn, Ni, Pb, and Zn*.

In studies of soil chemistry, in particular, of the migration and accumulation of elements in soils, the geological element classification is used (Goldschmidt, 1937). However, Vodyanitsky (2008) took notice of the shortcomings mentioning that this classification can only be used when considering the background environments but not the areas affected by human activity. He stressed the importance of soil properties when considering the behavior of trace elements in landscape environments. Soil is a polycomponental formation which comprises diverse groups of compounds which tend to bind trace elements in soil. At the same time, within this formation one element can be bound by several soil media such as organic matter or oxides/hydroxides. While in the geological element classification the majority of metals belong to a chalcophile group, in the soil element classification proposed by Vodyanitsky (2008) groups such as silicatophile, manganophile, and organophile were included (Tab. 1). So far, efforts to develop soil element classifications to be used in environmental monitoring are complicated by the lack of the knowledge about the behaviour of certain elements in soils.

Table 1: Chemical relation of metals according to geological element classification developed by Goldschmidt (1937) and soil element classification proposed by Vodyanitsky (2008).

	Element								
	As	Cd	Co	Cu	Hg	Mn	Ni	Pb	Zn
Geological classification (Goldschmidt, 1937)	C	C	S	C	C	S	S	C	C
Soil classification (Vodyanitsky, 2008)	S	O, M	M	O, M	C, O, A	ME	M, S	O, S, M	Sil, M (1); O, S (2)

S – siderophile;
C – chalcophile;
O – organophile;

M – manganophile;
ME – ore-forming element;
A – amalgamophil;

(1) – Automorphous soils;
(2) – Hydromorphous soils

2.1.2 General properties of trace metals and their behaviour in soils and plants

Trace metals are of natural origin. They are present in parent rock and occur in soils in the form of sulphides, oxides, silicates, and carbonates. The element abundance significantly varies in different types of parent rock material and depends on the mineralogical composition of rocks. The weathering processes of bed rocks lead to changes in their chemical composition. As a result of weathering processes, secondary minerals, hydroxides, and oxides tend to be the major

sources of trace metals (Il'yin, 1991). After being released into the environment, they can be adsorbed or chemically bound to natural substances, which influences the elements' ability to migrate (Dube et al, 2001). The mechanisms of leaching and migration of trace metals in soils vary depending on the element properties (e.g. ionic mass, ionic radius) (Bogdanovsky, 1994; Niskavaara et al, 1997). These mechanisms also depend on environmental conditions, in particular, on pH and soil redox potential (Fortescue, 1980). The migration intensity of trace metals in landscapes can be changed not only due to seasonal variation of local environmental parameters but also due to anthropogenic influence.

Plants are an important component of the biogeochemical cycle. The metal uptake by plants can be both external and internal. The first one is evident as deposition of the element on the leaves and stalks of plants. The internal metal input is caused by metals entering through the root system (Il'yin, 1991). The trace metal input to higher plants depends on the vascular tissues (phloem and xylem) as well as on evapotranspiration rate. Chelating ligands play an important role in transporting of trace elements in plants (Kabata-Pendias & Pendias, 2001). The element mobility is also determined by factors such as acidity, oxidation-reduction potential, element concurrence, hydrolysis, insoluble salt formation, plant species, and the stage of plant development. An excess of trace elements can be toxic in plants. Phytotoxicity can be expressed by plant growth inhibition, morphological changes such as chlorosis and necrosis, suppression of biomass accumulation, metabolic imbalance, reduction of photosynthesis processes and transpiration (Il'yin, 1991). However, some kinds of plant species are resistant to high amount of trace elements even without evident morphological changes (Isaev, 2004). Since the behaviour of trace elements depends on their properties and how they interact with the rock-soil-plant system, they are described in more detail in the following subsections.

Arsenic (As)

The natural sources of As in soils are mainly oxysalts and sulphur- containing minerals (O'Neil, 1995). Most arsenic containing minerals may be classified into one of five groups: elemental, arsenides, arsenosulfides, arsenites, and arsenates (Henke & Hutchison, 2009). The background levels of As in top soils are generally low and do not reach values higher than 10 mg kg⁻¹, although they exceed those in rocks several times. The lowest As levels are found in sandy soils and, in particular, in those derived from granites, whereas higher As concentrations are related

Chapter 2. State-of-the-Art

most often to alluvial soils and to soils rich in organic matter (Kabata-Pendias & Pendias, 2001). Although As minerals and compounds are readily soluble, As migration is greatly limited due to the strong sorption by clays, Fe, Al, or Mn oxy/hydr/oxides, and organic matter (Henke, 2009). Concentrations of As in terrestrial plants are generally low. Phytoavailability of As varies in different plant species and depends on the concentration of soluble As in soils (O'Neil, 1995; Kabata-Pendias & Pendias, 2001). Soil properties play a significant role in As plant uptake as well. Low soil pH values suggest an increase of As availability for plants when, for example, As-binding Fe and As oxycompounds become more soluble. However, more intensive uptake of As by plants may occur in higher soil pH (O'Neil, 1995). The most common symptom of As toxicity is growth reduction of plants. Other symptoms of As toxicity are described as leaf wilting, violet coloration (increased anthocyanin), root discoloration, and cell plasmolysis (Kabata-Pendias & Pendias, 2001).

Cadmium (Cd)

Cadmium is closely associated with Zn in its geochemistry. Both elements have similar ionic structures and both are strongly chalcophile, although Cd has a higher affinity for S than Zn (Alloway, 1995). Sedimentary rocks show a greater range of Cd concentrations than other rock types. Phosphorites and marine black shales are found with the highest Cd content. Both types of rocks are formed from organic-rich sediments under anaerobic conditions where trace metals accumulated as sulphides and organic complexes (Alloway, 1995). Most soils are expected to contain less than 1.0 mg kg^{-1} of Cd, except those contaminated by discrete sources or developed on parent materials with exceedingly high Cd contents (Alloway, 1995). Cd is known to be most mobile in acidic soils within the pH range of 4.5 to 5.5, whereas Cd is rather immobile in alkaline soils (Kabata-Pendias & Pendias, 2001). Within soil profiles, Cd is found being concentrated in the top horizon. In the zone with the highest organic matter content trace metals may be retained in this strongly adsorptive horizon after reaching it either as a result of cycling through vegetation or by wet and dry deposition from the atmosphere. It is suggested that Cd has no essential biological function (Adriano, 1986). However, being a trace element, it is readily translocated to the top of plant after sorption through the roots. pH is one of the major soil properties controlling both the total and a relative uptake of Cd (Kabata-Pendias & Pendias, 2001). Elevated Cd concentrations in plants can retard growth and damage root system. The

phytotoxicity of Cd can also show inhibitory effects on photosynthesis, disturb transpiration and CO₂ fixation, and alter the permeability of cell membranes (Kabata-Pendias & Pendias, 2001).

Cobalt (Co)

In the Earth's crust, the highest Co abundance is found in ultramafic rocks and to a lesser extent in sedimentary and acid rocks (Kabata-Pendias & Pendias, 2001). Co is allied to Fe and Mn in geochemical cycles. This element commonly has two oxidized states Co⁺² and Co⁺³. Under weathering conditions Co is relatively mobile in oxidized acidic media. Additionally, Co mobility in most soils is governed by Mn oxides and by pH-Eh soil properties (Kabata-Pendias & Pendias, 2001). However, it can be bound by Fe and Mn oxides, as well as by clay minerals (Isaev, 2004). Therefore, this element does not migrate in a soluble phase (Kabata-Pendias & Pendias, 2001). Co distribution in a soil profile is similar to Fe distribution in soil genetic horizons. However, in some cases the domination of Mn governs Co distribution in soils enriched by Mn minerals (Kabata-Pendias & Pendias, 2001). Organic matter and clay minerals are important factors controlling Co behaviour and distribution in soils as well. Clay minerals like montmorillonite and illite play a particularly important role in Co sorption (Kabata-Pendias & Pendias, 1989). Bound by organic matter, Co can easily be transported in soils in forms of organic chelates which can be available to plants. Soil pH seems to be a significant factor governing Co phytoavailability (Smith & Paterson, 1995).

Copper (Cu)

Cu in the Earth's crust is most abundant in mafic and intermediate rocks and has a tendency to be excluded from carbonate rocks (Baker & Senft, 1995; Kabata-Pendias & Pendias, 2001). It forms several minerals of which the common primary minerals are simple and complex sulphides. These minerals are easily soluble in weathering processes and release Cu ions, especially in acid environments. Cu cations tend to interact chemically with minerals and organic soil components, therefore Cu is one of the least mobile elements in soils (Baker & Senft, 1995). The most stable forms of Cu in soils can be formed due to binding of this element with hydroxides of Al and Fe. In addition, a great number of organic compounds, particularly humic and fulvic acids are likely to form stable complexes with Cu when it is present in small amounts. The common characteristic of Cu distribution in soil profiles is its accumulation in the top horizons. Among

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other functions, Cu concentration in surface soils reflects the bioaccumulation of the metal (Kabata-Pendias & Pendias, 2001). Transport of Cu to plants occurs in low amounts. The distribution of this element in plants is not clearly predictable as well. For example, forms of Cu in plant roots are immobile and found in cell walls. The highest concentration of Cu is always observed along with the phase of intensive growth (Kabata-Pendias & Pendias, 1989). The phytotoxicity of Cu in plants is shown, for example, as chlorosis and tip necrosis of leafs and changes in the permeability of the cell membranes (Alloway, 1995).

Iron (Fe)

Fe is one of the abundant elements in the lithosphere and concentrates primarily in igneous rocks. Thus, Fe content in soils is determined by its presence in the parent material and additionally by the nature of soil processes. Fe behaviour in soils is strongly associated with oxygen, sulphur, and carbon geochemical cycles. Oxidation and alkaline conditions facilitate Fe precipitation whereas reduction and acidic conditions lead to solubility of Fe compounds (Vodyanitsky, 2003). Oxides and hydroxides of Fe are the predominant compounds of this element occurring in forms of small particles in organic-rich soil horizons. In the form of hydroxides and oxides Fe can replace Mg and Al in other minerals and form complexes with organic ligands. Mineral and organic forms of Fe can easily be transformed in soils. However, organic matter significantly affects the formation of Fe oxides. At the same environmental conditions, these compounds can occur in amorphous, semi-crystalline and crystalline forms (Kabata-Pendias & Pendias, 2001). Occurrence of oxides/hydroxides of Fe in the soil matrix in humid landscapes is a very important factor which affects the gleying processes development and, therefore governs physical and chemical soil properties (Vodyanitsky, 2010). Fe is essential for most organisms. Oxidation or reduction of Fe-ions or its compounds, as well as formation of Fe complexes are effective in biochemical reactions without changing the valence of Fe (Murad & Fischer, 1988; Vodyanitsky & Dobrovolsky, 1998). Uptake of Fe by plants and its transport in vegetative organs depend on plant development and environmental factors such as pH, calcium and phosphorus content, and trace element relationship. At neutral soil pH levels, Fe organic complexes play an important role in plant nutrition. Fe is not readily transported in plant tissues. Therefore, its deficiency appears first in younger plant parts. Fe tolerance of plants is often associated with oxidation and immobilization and/or exclusion of soluble Fe by roots.

Plants adapted to waterlogged conditions are commonly more tolerant to high Fe levels than plants grown in well-aerated soils (Kabata-Pendias & Pendias, 2001).

Mercury (Hg)

Abundance of Hg in the Earth's crust is uncertain. Hg occurs in several ionic forms. However, it is not very mobile during weathering. Affinity to be bound with S (e.g. HgS), formation of stable organomercury compounds in aqueous media, and volatility of Hg are the most important geochemical characteristics of this element (Kabata-Pendias & Pendias, 2001). Hg occurs naturally in soils at concentrations ranging from a few $mg\ kg^{-1}$ to few hundred $mg\ kg^{-1}$. Below the surface level, Hg is fairly mobile in the soil profile, and it tends to accumulate in the surface horizons. The Hg content of a given soil horizon could be related to clay content and/or the organic matter of that horizon (Adriano, 1986). Sorption of Hg by clays in soils seems to be relatively limited and varies little with soil pH (Steinnes, 1995). The accumulation of Hg is controlled by organic complex formation and by precipitation (Kabata-Pendias & Pendias, 2001). In general, the phytoavailability of Hg is low. However, the root system tends to accumulate Hg acting as a chemical barrier (Steinnes, 1995).

Manganese (Mn)

Mn is one of the most abundant elements in the lithosphere. The cation Mn^{+2} is the most common form in rock-forming silicate minerals. This cation tends to displace some bivalent cations in silicates and oxides. Mn can form a variety of oxides and hydroxides which create continuous series of compounds with stable and unstable atomic configuration. Mn compounds play a significant role in the soil properties because this element regulates the behaviour of other micronutrient elements. Besides, Mn affects soil properties such as the pH-Eh equilibrium. The reducing and acidification of Mn compounds may be very fast and depends on soil properties. Therefore, oxidizing conditions can significantly decrease the uptake of Mn, whereas reducing conditions may increase the element uptake and Mn concentrations in plants up to toxic amounts (Kabata-Pendias & Pendias, 1989). Mn is an important microelement for plants. The element participates in photosynthesis reactions, increases sugar content, and intensifies plant respiration rates (Vodyanitsky, 2009; Vodyanitsky et al, 2012). Plant uptake of Mn occurs via metabolic processes in the form of other bivalent cations. Plants tolerant to excess amount of Mn can

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accumulate this element in root tissues or precipitate it in the epidermis in form of MnO_2 (Kabata-Pendias & Pendias, 1989). Toxicity of Mn is developed under water-saturated and low redox potential conditions. The most common effects of toxic Mn concentrations are ferrous chlorosis, necrotic dark spots on leaves, corrugation of a limb, and random distribution of chlorophyll in leaves.

Nickel (Ni)

According to its geochemical properties Ni is a siderophile element and therefore, strongly associated with Fe. Its concentration decreases with increasing acidity of rocks (Kabata-Pendias & Pendias, 2001). In terrestrial rocks, Ni occurs primarily in sulphides, arsenides, and antimonides. Under weathering conditions Ni is easily mobilized and co-precipitated with Fe and Mn oxides (McGrath, 1995). Ni distribution in soil profiles is related either to organic matter content or to amorphous oxides and clay fractions, depending on soil types. Organic matter has a strong ability to adsorb Ni. Therefore, this metal is likely to be concentrated in coal and oil (Kabata-Pendias & Pendias, 2001). However, soil pH seems to be the most important factor affecting the distribution of Ni between the solid and liquid phases in soils rather than the clay content and the amount of Fe and Mn oxides and hydroxides (McGrath, 1995). Ni content varies significantly in plants that grow on background areas and depends on biological and environmental factors. The tendency to uptake this element depends on both soil and plant characteristics. However, the soil pH plays the most important role in Ni uptake. This element can easily be removed from soils by plants and concentrated either in leaves or in seeds. This element can likely be toxic for plants growing on acidic soils. Excess amount of Ni may result in damage of plants. Before the symptoms of toxicity become evident, high amounts of Ni inhibit processes of photosynthesis and transpiration, and slowdown molecular nitrogen fixation by plants (Kabata-Pendias & Pendias, 1989).

Lead (Pb)

Among trace metals regardless Fe and Mn, Pb is one of the most abundant in the earth's crust. Pb occurs mainly as Pb^{+2} , although it may also be found in the oxidation state Pb^{+4} , and it forms several other minerals which are quite insoluble in natural waters. This metal has highly chalcophilic properties (Goldschmidt, 1937; Adriano, 1986). During weathering, Pb sulphides

slowly oxidize and have the ability to form carbonates and also to be incorporated in clay minerals, in Fe and Mn oxides, and in organic matter. The natural Pb content of soil is inherited from parent rocks. Pb is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides, and organic matter. A high soil pH may cause Pb precipitation as hydroxide, phosphate, or carbonate forms, as well as promote the formation of rather stable Pb-organic complexes. Increasing acidity may increase Pb solubility, but this mobilization is usually slower than the accumulation in the organic-rich layer of soils (Kabata-Pendias & Pendias, 2001). The characteristic accumulation of Pb near the soil surface in most soil profiles is primarily related to the accretion of organic matter in the surface soil layer. Therefore, organic matter should be considered as an important sink of Pb in polluted soils (Bolshakov et al, 1978; Kabata-Pendias & Pendias, 2001). Pb is neither an essential nor a beneficial element for plants. Methods of Pb uptake by plants are passive. Despite poor solubility of Pb in soils, this element is taken up by root fibrils and bound in cell walls (Davies, 1995).

Zink (Zn)

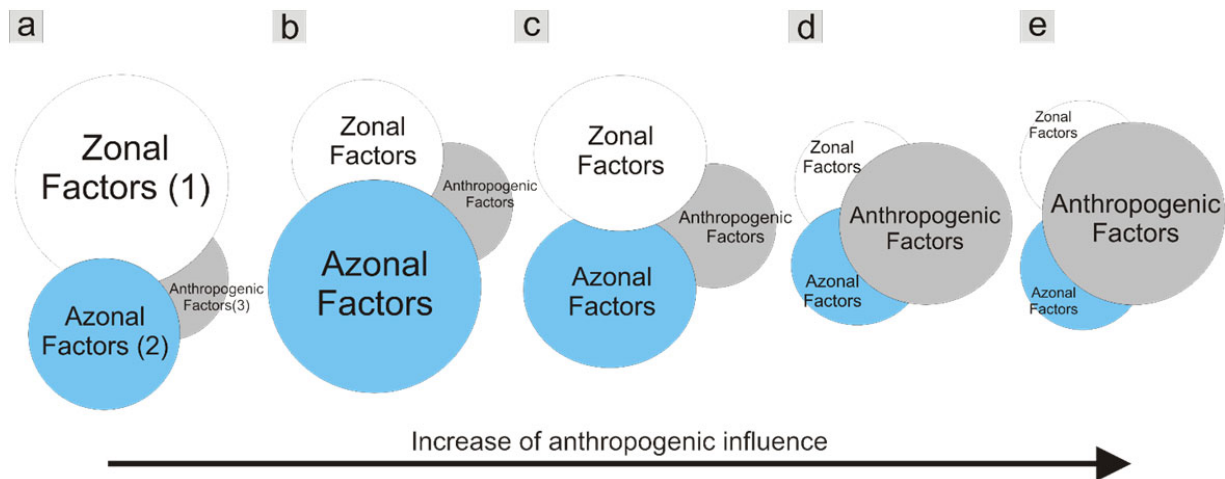
The most abundant sources of Zn are the ZnS minerals. The total Zn content of soils largely depends on the composition of the parent rock material. In sedimentary rocks, the highest Zn contents are found in shales and clayey, while sandstones, limestones, and dolomites have generally lower contents. In soils, Zn is associated with hydroxides of Fe and Al (14 – 38 % of the total Zn content), and with clay minerals (24 – 63 % of the total Zn content). Mobile forms and organic complexes of Zn in soils contribute only 1 – 20 % and 1.5 – 2.3 %, respectively. Therefore, accumulation of this element is observed in organic-rich horizons and peat material where Zn occurs mainly in colloidal forms (up to 60% of the total element content) (Kabata-Pendias & Pendias, 2001). The common and less specific indications of Zn toxicity for plants are growth inhibition, suppression of biomass accumulation, leaf chlorosis and necrosis (Alekseeva-Popova, 1991).

2.1.3 Assessment methods of trace metal background levels in soils

Background monitoring of the environment is an important part of the global scale monitoring (Izrael, 1982; Izrael & Rovinsky, 1988). The knowledge about background levels of trace elements in soils plays a key role in estimating possible changes of the environment caused

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mainly by human activity. At present, background areas are considered to be zones where anthropogenic impact is minimal (Fig. 2).



(1): Includes zoning of climate, natural waters, soils, vegetation and etc.;

(2): Includes remoteness from the ocean, differentiation of geological structure, relief and etc.;

(3): Includes all kinds of human impact (e.g. industrial emissions, mining operations, deforestation and etc.)

Figure 2: Importance of zonal and azonal factors in biogeochemical cycles for areas which have undergone various extent of anthropogenic influence: (a) – background areas, (b) – undisturbed areas with natural geochemical anomalies, (c) – weakly disturbed areas undergone local pollution sources, (d) – disturbed areas with technogenic anomalies, and (e) – metropolitan agglomerations (slightly modified after [Movchan & Opekunova, 2002](#)).

In order to estimate background levels of trace metals in natural landscapes, many studies proposed to use the average composition of the upper continental crust (so-called “*clarke values*”; [Taylor, 1964](#); [Alekseenko, 1990](#); [Il’yin, 1991](#); [Kabata-Pendias & Pendias, 2001](#)). In several publications it is suggested to compare the analytical soil data with published global or world soil average values ([Vinogradov, 1957](#); [Bowen, 1979](#)). This method requires knowledge of the total element content in soils. However, the investigations of [Caritat et al \(2012\)](#) showed that the comparison of the data with average crustal values and world soil averages may lead to errors. The authors found substantial differences between the published world soil averages and their median element concentrations observed on two continents. They stated that little relation exists between the spatial distribution of lithological units and the observed soil chemistry. The

authors pointed out that trace metal background levels in soils depend not only on mineralogic, petrographic, and geochemical characteristics of parent rock material but also on the climatic characteristics and related processes which are often not taken into account. Another approach is based mainly on studies of the element distribution in soils, features of element migration and accumulation in a landscape. The criteria of the assessment of the background element distribution were described in studies of [Perel'man \(1975\)](#) and [Glazovskaya \(1988\)](#) and include so-called coefficients of radial and lateral disparity, coefficients of biological uptake and other. However, since various methods are used to estimate the element background levels, a comparison among different datasets remains difficult.

Many authors point to the necessity of environmental monitoring on regional and local scales ([Il'yin, 1991](#); [Prokhorova & Matveev, 1996](#); [Motuzova, 2001](#); [Motuzova & Bezuglova, 2007](#), [Motuzova & Karpova, 2013](#)). So far, one of the ecosystem approaches of environmental monitoring which has been developed in Russia is a conceptual design of ecological standardization. Within the framework of this approach, so-called approximate permissible concentrations (APC) were developed ([Hygienic standards, 2009](#)). The aim of this standardization is to receive a more complete idea of soil contamination by inorganic pollutants. Values of APC for chemical elements of natural origin were calculated for three groups of soils with different physical and chemical properties. To some degree, these values help to determine a buffer capacity of soils and consequently, a soil resistance to pollution (Tab. 2). However, some authors note (e.g. [Dabakhov et al, 2005](#); [Vodyanitsky, 2013](#)) that this method cannot serve as a flexible way for estimating the extent of soil pollution because these values are established only for certain elements and do not take into account the entirety of soil properties. Therefore, the method may serve only as a guideline in estimating background levels of trace metals in soils. Another approach in environmental assessment of soils was developed in Germany by the Ministry for the environment and consumer protection ([LABO, 2003](#)). According to this method, background element values in soils (so-called “*Hintergrundwerte*”) are determined for all territorial districts taking into account background concentrations (so-called “*Hintergrundgehalt*” defined as parent material and nonpoint element input), type of soil horizon, and land use. These values are statistically verified. For example, Table 3 shows the background element values in various soil materials of the forested area in northeast Germany.

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Table 2: Approximate permissible concentrations (APC) of selected trace elements and metalloids in soils with various physical and chemical properties (Hygienic standards, 2009).

Soil group (based on soil texture)	APC with account of background (mg kg ⁻¹)					
	As	Cd	Cu	Ni	Pb	Zn
1	2.0	0.50	33	20	32	55
2	5.0	1.0	66	40	65	110
3	10	2.0	132	80	130	220

- 1 - Soils of sandy and sandy loam texture
 2 - Acidic soils (sandy loam and clay) with pH < 5.5
 3 - Soils inclined to neutral (sandy loam and clay) with pH > 5.5

Table 3: Average background concentrations of the selected elements (percentile of 90) determined for soils of northeast Germany. The data is shown for the surface and bottom horizons of various types of soil material (LABO, 2003).

	Element concentration in mg kg ⁻¹ (AR)				
	Cd	Cu	Ni	Pb	Zn
<i>Surface horizons</i>					
Sand (Forest soils, northeast Germany)	0.32	8.5	6.9	41	25
Peat (Greenland organic-rich soils, northeast Germany)	0.40	26	10	48	50
<i>Bottom horizons</i>					
Sand	0.24	7.0	9.4	12	24
Peat	0.49	18	22	22	33

A further approach of environmental monitoring is based on statistical methods. Some studies suggest (e.g. [Motuzova, 2001](#)) that background levels of an element in an environmental media can be considered as a sum of the natural element content inherent the area, and a contribution due to long-range atmospheric transport. The statistical technique, so-called “*three-sigma rule*”, can be applied when one considers that the element distribution in soils of background areas is governed by the Gaussian probability law. This technique allows estimating the maximum natural element concentrations in soils. The upper boundary of an average element concentration in soils is the value which exceeds the average regional background level on three-sigma limits ($\mu+3\sigma$). It covers 99 % of the studied components. The aim of this method is to determine the regional natural contents of chemical elements in soils taking into account their natural variation. The significant exceedance of the upper boundary of an average element concentration is determined as the deviation from the average element content. In studies of [Reimann et al \(2005\)](#) using the concept in exploratory geochemistry the element background concentrations were correspondent to the values ranging from “median \pm 2 maximum absolute standard deviation

(MAD)”. In this method the value of “median + MAD” is determined as the upper limit of the geochemical background called “threshold level”.

2.1.4 Sources and pathways of trace metals in the Arctic

The Arctic environment is affected by various pathways of trace element input (AMAP, 2005). Considerable amounts of pollutants can reach the Arctic through the atmosphere as the fastest and the most direct transport way. The majority of trace elements enter to the atmosphere from natural sources such as aeolian dust, chemical and biological volatilization, geothermal activity, volcanic eruptions, and others. Volcanic releases to the atmosphere can contribute 40 to 50 % of Cd and Hg, and 20 to 40 % of the As, Cu, Ni, and Pb of the total emission (Kiekens, 1995). However, some studies showed that aerosols containing trace elements of anthropogenic origin can be transported within air masses from the midlatitudes (e.g. Jaworowski et al, 1981; Barrie, 1990; Klaminder et al, 2011) and be trapped in the atmosphere of the Arctic region, particularly during the winter period (Ottar, 1981; Djupström et al, 1993). Three trace elements, namely Hg, Pb, and Cd mainly contribute to emissions of anthropogenic origin to the atmosphere (e.g. Macdonald et al, 2000; AMAP, 2005; Fitzgerald et al, 2005; Liu et al, 2012). Local anthropogenic sources in the Arctic region significantly contribute to trace metal deposition from the atmosphere. The direct anthropogenic influence on Arctic ecosystems was demonstrated in many studies which were conducted in the Russian Arctic and sub-Arctic. Metal levels in environmental media were determined around or nearby big industrial complexes such as the Norilsk copper-nickel industry in western Siberia (Gytarsky et al, 1995; Ziganshin et al, 2011), industrial complexes in Kola Peninsula (Nikonov & Lukina, 1996; Boyd et al, 1997; Reimann et al 1999; Opekunova et al, 2006, 2007), and Pechora River Basin (Walker et al, 2006). These and many other sources of industrial pollution do not only have a local environmental impact but they also contribute to the global long-distance pollution of the atmosphere brought to the Arctic (Vinogradova, 2000; Liu et al, 2012). In studies mentioned in AMAP assessment report (AMAP, 2005) the riverine input and sea ice were pointed out as other possible pathways for metal transport to the Arctic. In particular, Hölemann et al (2005) reported the significance of the spring freshet of arctic rivers which increases dissolved trace metal fluxes to the Arctic Ocean. According to Pokrovsky et al (2012) the majority of the metal flux which occurs during the spring flood may contribute up to 60 to 80 % of the total water discharge to the Arctic Ocean. In

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the opinion of Dobrovolsky (2004) insoluble compounds play the crucial role in the metal transport by rivers, in particular fine-grained soil particles. Nevertheless, metal fluxes in Siberian rivers are comparable or even less than those found in most major rivers worldwide (Alexeeva et al, 2001; Gordeev, 2009). Some authors (e.g. Lisitzin, 1994; Khlebovich et al, 1997) draw attention to the study of estuarine ecosystems particularly the Arctic river deltas as the mixing zones are prone to contaminant accumulation and dissipation. Pfirman et al (1995) noted the importance of sediments and organic matter incorporation into sea ice as a contributor to pollutant transport in the Arctic.

It was reported in the AMAP assessment report (AMAP, 2005) that possible changes in trace metal pathways may occur due to predicted climate change. The reconstruction of the climatic impact of Pb pollution in lake sediments at Spitsbergen was done by Liu et al (2012). The authors assumed that the absence of a signal of Pb pollution in the surface lacustrine sediments could be due to enhanced climate-sensitive processes such as surface erosion, precipitation and others caused by a warming effect in Arctic regions. Pokrovsky et al (2012) concluded that among several factors affecting the increase of trace element fluxes in high latitudes due to climate warming, the plant productivity and community composition would play the most important role.

2.2 Permafrost-Affected soils

2.2.1 Introduction

The most important effect of the continental climate is a distribution of permafrost within the Arctic region. It is found under approximately 25 % of the land surface of the Northern Hemisphere (Turner & Marshal, 2011). According to Soil Survey Staff (2010) permafrost is defined as the temperature regime, in which soils and sediments remain at or below 0 °C for at least two consecutive years. It was initially applicable to perennially frozen ground. However, this definition is given only on the basis of the temperature but not on the freeze-thaw state or a composition of the ground. Permafrost can be divided into continuous, discontinuous, sporadic, and isolated (Brown et al, 1998). This division is based on the permafrost occurrence within the areas of the northern circumpolar region (Fig. 3). Beside the high latitudes, permafrost is also found in mountainous regions and plateaus of high altitudes in middle and low latitudes. In the

Antarctic, permafrost zones are restricted to coastal lowlands of the Antarctic Peninsula and its offshore islands and occupy only 0.35 % of the region (Bockheim et al, 2008).

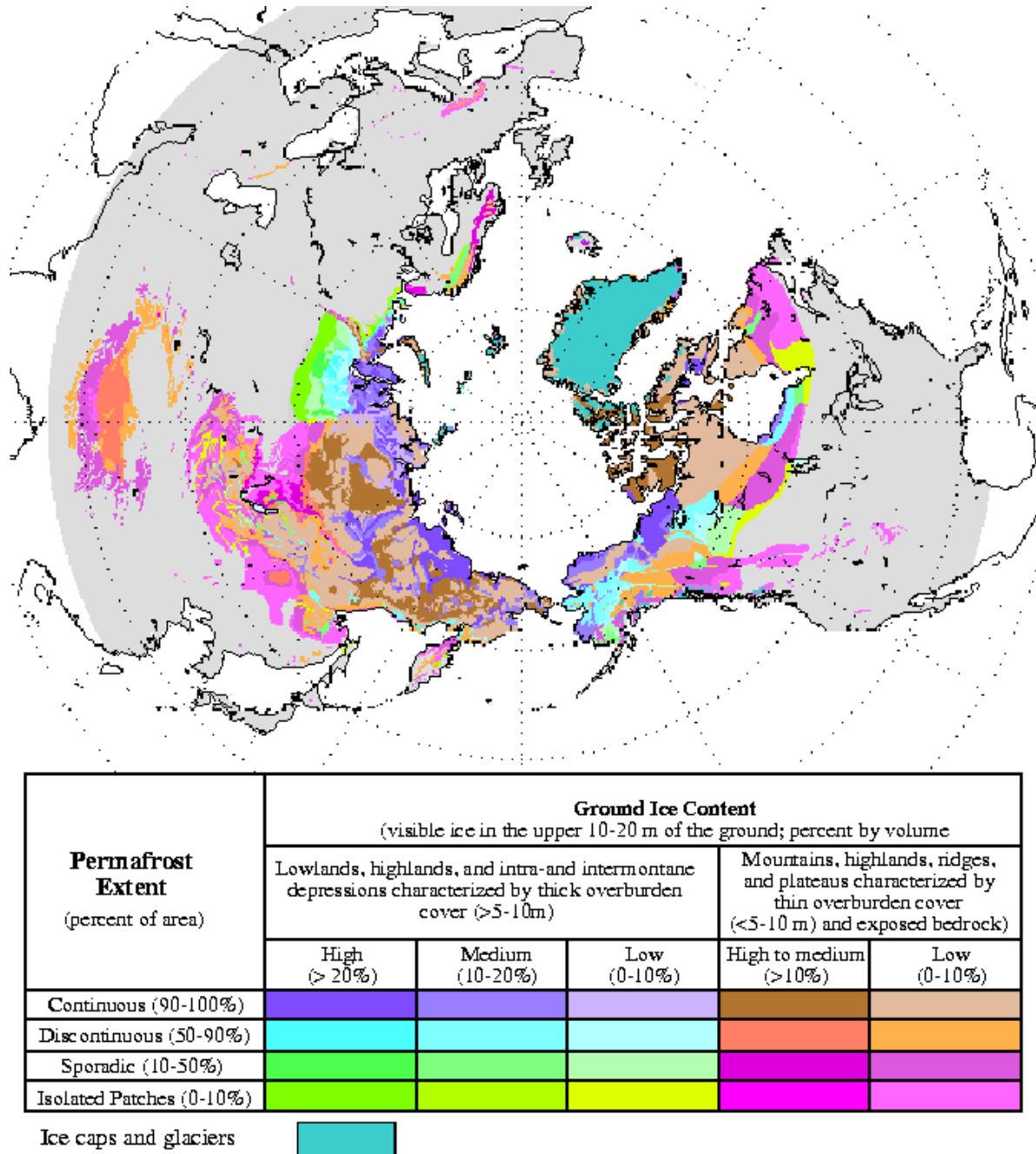


Figure 3: Different types of permafrost in the northern circumpolar region (Brown et al, 1998). Violet and brown colours represent the distribution of continuous permafrost of lowlands and mountain areas, respectively.

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Permafrost-affected soils cover approximately 180×10^6 km² of the global land area of the Northern Hemisphere (Soil Survey Staff, 2010). Relief features, discontinuity of the snow cover, wind pattern, and soil water regime result in a great variety of permafrost-affected soils (Vasilyevskaya et al, 1993; Goryachkin, 2010). Apart from the factors mentioned above, a wide variety of parent materials contributes to a great diversity of these soils developed in the Arctic region. The following soil forming processes dominate in the Arctic zone and affect the soil profile development: (1) organic matter accumulation, (2) cryogenesis, and (3) gleization. A large amount of organic carbon in both the active and deeper perennially frozen horizons is one of the unique properties of permafrost-affected soils (Tarnocai, 2006; Ping et al, 2008). In permafrost-affected soils, the total organic carbon pool amounts to 1024 Pg (Tarnocai et al, 2009). According to investigations carried out in the Lena River Delta of northeast Siberia, the mean soil organic carbon stock for the upper 1 m of soils of the Holocene terrace has been estimated to be $29 \text{ kg m}^{-2} \pm 10 \text{ kg m}^{-2}$ (Zubrzycki et al, 2013).

2.2.2 Physical and chemical properties of permafrost-affected soils

Permafrost-affected soils show a great variety of physical and chemical properties which was described in detail for soils of the Alaskan (e.g. Everett & Brown, 1982; Ping et al, 1998), Canadian (e.g. Pettapiece, 1975; Walker, 2012), and Russian Arctic (e.g. Vasilyevskaya et al, 1986; Lupachev & Gubin, 2008). Permafrost plays a significant role in landscape morphology formation as well as in processes of soil formation. The main soil forming processes which specify the surface morphology of permafrost-affected landscapes are freezing and thawing, cracking, frost heave, frost stirring, mounding, fissuring, and solifluction. As a result of cryopedogenesis, patterned ground such as non-sorted circles, stripes, so-called medallion spots, hummocks, and ice wedge polygons occur (Fig. 4). The repeating cycles of freezing and thawing lead to cryoturbation (frost churning) that includes irregular or broken horizons (Fig. 5) and an incorporation of organic matter and other inorganic compounds, especially along the top of the permafrost table (Tarnocai & Smith, 1992; Bockheim & Tarnocai, 1998). The permafrost occurrence in the deepest mineral soil horizons often results in waterlogging of the permafrost-affected soils. Under these conditions, the processes of gleying and other redoximorphic properties are predominant.

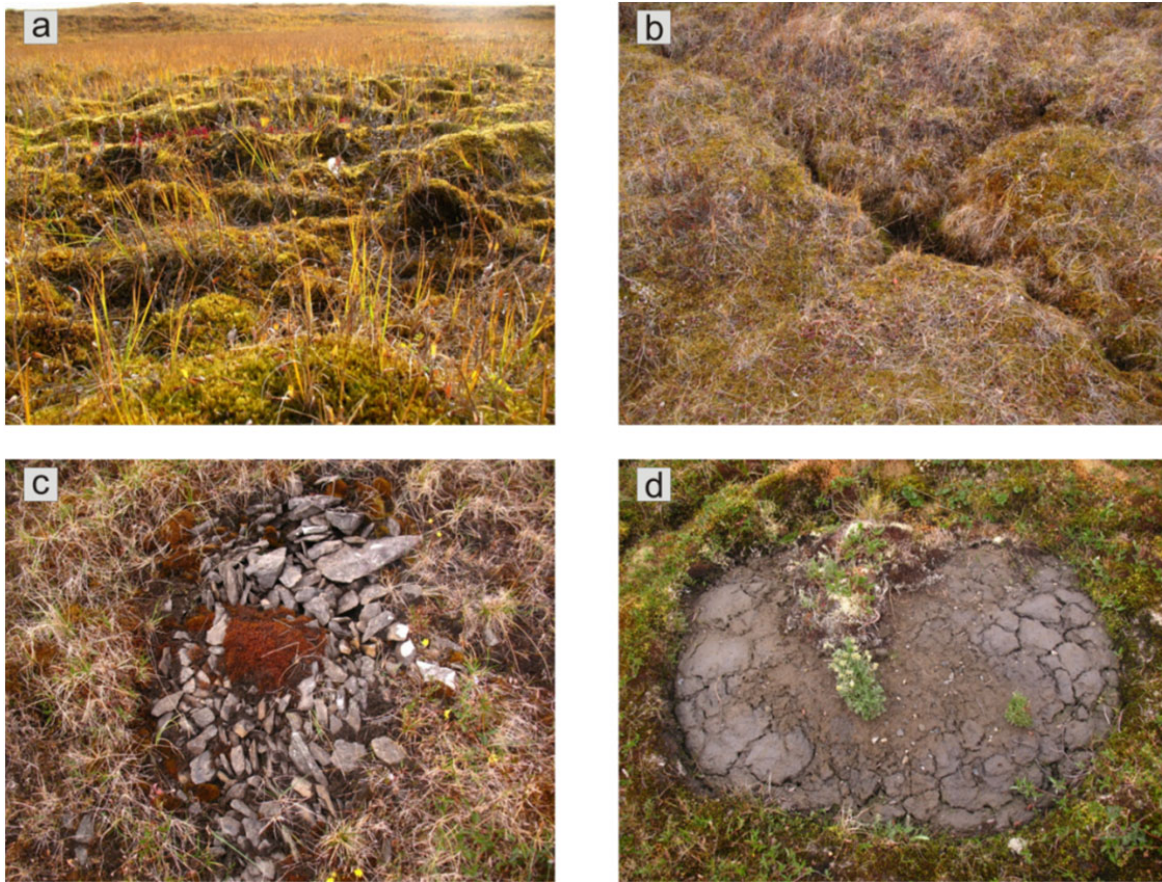


Figure 4: Examples of permafrost patterned ground governed by individual natural and climatic characteristics of the Arctic region: (a) – Hummocks and (b) – frost cracks (landscapes of Samoylov Island, the Lena River Delta); (c) – sorted and (d) – non-sorted circles as the result of the frost heaving on the area of Tiksi. Own photos (2011).

Most permafrost-affected soils display a wide range of pH from strongly acidic to slightly alkaline reaction, from low to high basic saturation, the dominance of carbonates and exchangeable ions. In studies of [Tedrow \(1968\)](#) and [Ugolini \(1986\)](#) was mentioned that the existence of gradients in environmental characteristics and related chemical processes may result in pronounced soil zonation in the Arctic region. Occurrence of permafrost, and thus a complex system of the soil forming processes developed in Arctic soils under the influence of climatic conditions, affects the features of geochemical processes that occur there. [Sokolov et al \(1997\)](#) suggested that hydrogenic conditions of permafrost-affected soils are the most important factor which results in washout of soil-forming components (i.e. soil mineral particles, exchangeable ions). Studies of [Chagué-Goff & Fyfe \(1997\)](#) showed a strong influence of permafrost

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occurrence on the element distribution within the peat profile. An enrichment of all analysed trace elements was observed directly above the permafrost table and a depletion directly below, independent of their association with the mineral or organic compounds. The authors suggested that the seasonal freezing and thawing processes affected the solute redistribution within the soil profile. The investigation of [Schuster et al \(2004\)](#) showed that the presence of permafrost greatly influences on the transport of dissolved organic matter (DOC) which is capable to bind many elements and moreover, enhances their transport.

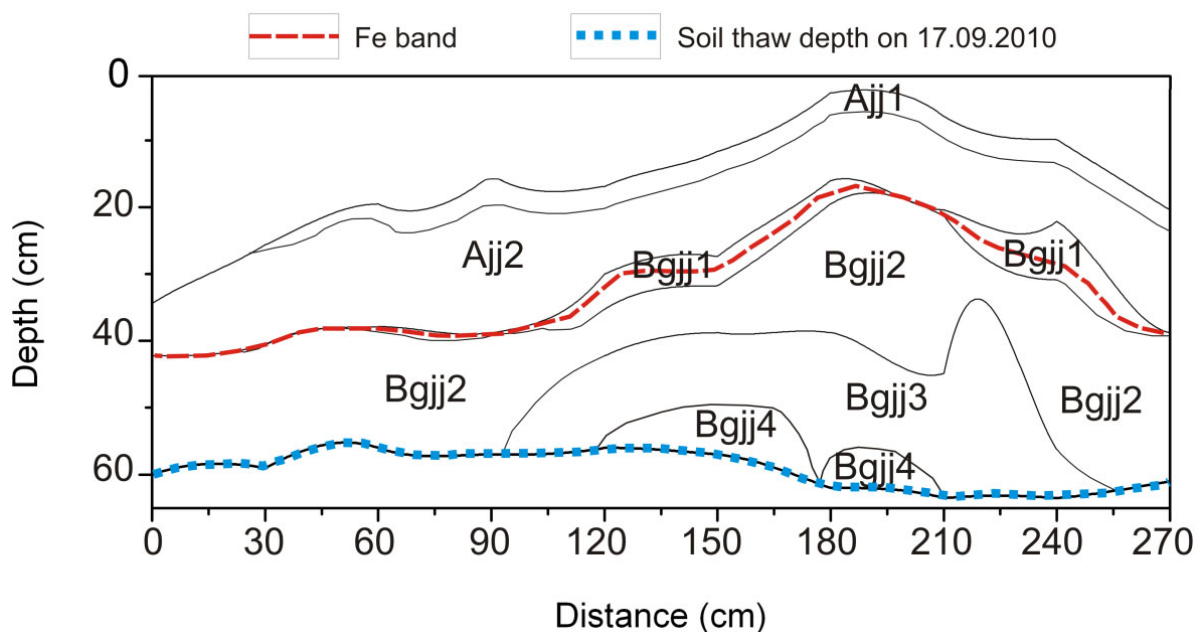


Figure 5: The soil profile of a cryoturbated soil of the polygon rim at the first terrace of Samoylov Island (the Lena River Delta, northeast Siberia). Scheme composed from field observations (17.09.2010). Soil horizon indexes identified according to the US Soil Taxonomy ([Soil Survey Staff, 2010](#)) where the index “A” indicated a mineral horizon which was formed at the soil surface or below an organic horizon, the index “B” indicated subsurface mineral horizons. The suffix “jj” indicated the cryoturbation occurrence. The suffix “g” characterizes the horizons with gleying properties.

2.2.3 Mechanisms of trace element distribution in permafrost-affected soils

Trace metals in soils occur in both mobile and bound forms. The migration of soluble elements in soils is governed by a number of physical and chemical processes, including advection,

diffusion, and dispersion. Further processes influencing the distribution of dissolved and particulate metals in soils are precipitation, adsorption, organic complex formation and ligand exchange (Fig. 6). For example, the mass transfer can be a potentially important mechanism for Hg and As. These elements can be moved out of the system by leaching to ground water, volatilization, or plant uptake (McLean & Bledsoe, 1992). The behaviour of trace metals in soils may differ from the free ion migration because of the ability of metals to form soluble complexes with other soil compounds (e.g. organic and inorganic ligands). The presence of complexes in the soil solution may strongly affect the element transport in soils. Because the metal complexes may be of varied valency (positively/negatively charged or electrically neutral), the adsorption of these complexes by soil may be weaker or stronger relative to the free metal ion (McLean & Bledsoe, 1992; Robinson et al, 2005).

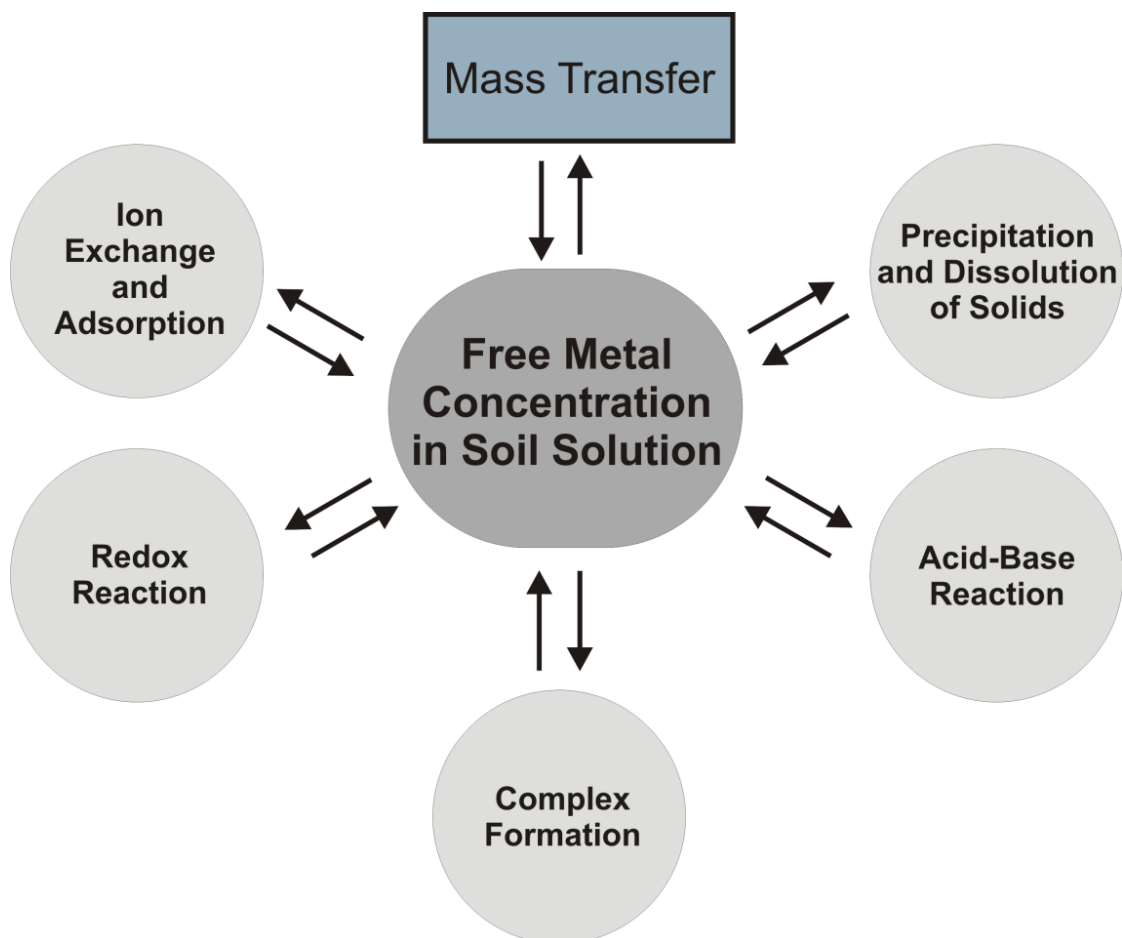


Figure 6: A scheme of processes which control free trace metal concentration distribution in soil solution (Mattigod et al, 1981).

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It is necessary to note that in permafrost-affected soils, apart from the processes mentioned above, the freezing process may significantly influence on the element distribution within the soil profile. Many studies, focused on the physical processes occurring in permafrost-affected soils, showed that the occurrence of a strong temperature gradient affects the heat and water transfer within the soil profile (Hoekstra, 1966; Hoekstra, 1967; Cary & Mayland, 1972; Cary, 1987; Shoop & Bigl, 1997; Sheshukov & Egorov, 1998; Boike et al, 2008; Nagare, 2012).

The mechanism of the soil water transport in freezing soils is based on the capillary model and shown in Figure 7. The main idea of this model is based on the relationship between cryosuction and water content in frozen soils which reflects the pore size distribution in soils. The cryogenic suction can be called a pressure deficit or a negative pressure and it is determined as a function of the latent heat of fusion (amount of heat energy which is released when the change of water state occurs at the freezing point 0 °C) and the temperature. The temperature gradient in permafrost-affected soils remains regardless of the seasonal change of its direction during autumn and spring. During autumn the decrease of the heat input to the surface soil horizons permits not only the downward freezing from the top soils but also the upward freezing of the active layer from the permafrost table. Within the soil profile, water begins to migrate along the water films adsorbed to the soil particles from the unfrozen side to the frozen side. When the soil begins to freeze, the water that is least attached to the soil particles by capillary forces and adsorption freezes first. The freezing of water leads to ice crystal formation in the soil pore spaces (Hoekstra, 1966; Konrad & Morgenstern, 1980; Sheng et al, 1995). The ice lenses grow through the supply of liquid water from the unfrozen soil area. The advance of the freezing front in the soil profile depends on the soil particle pore size distribution and the relevant radius of capillaries at the ice-water interface ($r_{\text{ice-water}}$). If the radius $r_{\text{ice-water}}$ is smaller than the minimum pore space size r_{pore} , the ice lens continues to grow, otherwise the freezing halts (Fig. 7b).

In frozen soils, the movement of water occurs mainly through water films adsorbed by the soil particles therefore, the water films may transport metal ions. A survey of literature showed that there are in situ studies dedicated to redistribution of soluble components in permafrost-affected soils (Panin & Kazantsev, 1986; Ostroumov et al, 1998; Ostroumov et al, 2001; Streletskii et al, 2003). The processes of water and salt migration and interactions between freeze-thaw processes and selected chemical elements in soils were studied in detail (Cary & Mayland, 1972;

Chamberlain, 1983; Henry, 1988; Marion, 1995). A few experiments focused on transport and fate of trace metals in frozen soils and were demonstrated in studies of Chuvilin et al (1998) and Lund & Young (2005). Therefore, experimental studies are required to understand the processes of the metal transport in soils affected by frost.

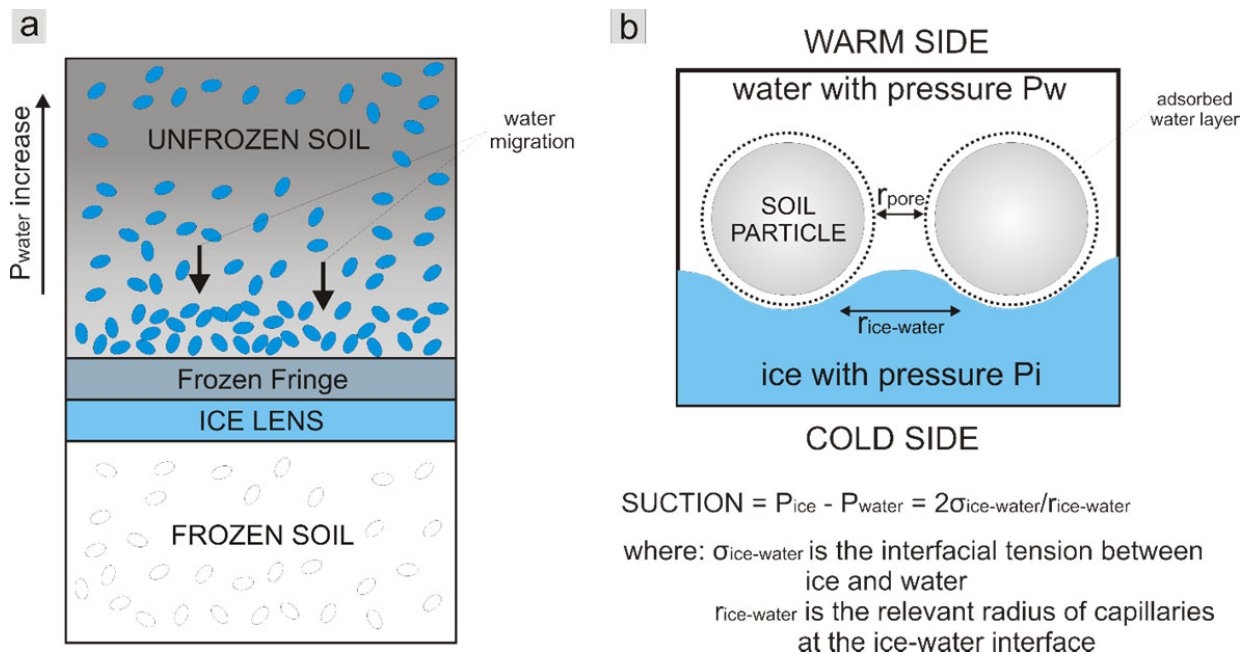


Figure 7: A schematic diagram showing the capillary model of segregation ice formation. According to this model, segregation ice forms when the freezing front halts – (a); ice would penetrate through the soil particles if $r_{ice-water} < r_{pore}$. The freezing front would halt if $r_{ice-water} > r_{pore}$ – (b); According to the Clausius-Clapeyron equation, the increase of suction can be determined as difference between the ice pressure (P_i) and the water pressure (P_w) and causes the water migration to the freezing front (modified after Davis (2001) and Woo (2012)).

2.2.4 Different approaches of classification of permafrost-affected soils

The processes indicated above contribute to the variety of classification approaches of permafrost-affected soils. At present, four schools of soil science are developed and used to classify permafrost-affected soils: the Russian, Canadian, American (US Taxonomy), and the World Reference Base for Soil Resources (FAO/UNESCO). Each of them is based on its own system of soil diagnostics and classification. The features of each classification system are described in following subsections.

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Russian soil classification

About 65 % of the land area in Russia is occupied by permafrost-affected soils (Makeev, 1993; Brown et al, 1998). Despite the wide spatial distribution and early studies of Russian scientists as Docuchaev, V. V., Sibirtsev, N. M, Krasuyk, A. A., Zolnikov, V. G., and others on permafrost-affected soils, they were not included in the official soil classifications of the former Soviet Union called “Guidelines for classification and diagnostics of soils” (Rozov & Ivanova, 1967) and “Classification and diagnostics of USSR soils” (Egorov et al, 1977) because of soil data limitation for northern regions. According to Dobrovol’sky & Trofimov (1996) and Goryachkin (2003), one of the important drawbacks of the official Soviet Union soil classification was that it disregarded the soils developed on the so-called areas of risk farming. At the same time, taxonomies of permafrost-affected soils were developed on a nationwide scale (Ivanova, 1976; Elovskaya, 1987; Kovda & Rozanov, 1988) and were based on the same fundamental approaches used in the soil classification of the Soviet Union: factors of soil formation, processes, and characteristics of soils. The latest Russian classification system was considerably improved when compared to the previous edition. To describe permafrost-affected soils, in this Russian soil classification (Shishov et al, 2004) two orders were defined: (1) *cryometamorphic soils* and (2) *cryoturbated soils* instead of one order called *Cryozem*. The first order joins the groups of soils which are developed primarily on sandy and medium-textured loam deposits and characterized by occurrence of both an organic horizon and a cryometamorphic horizon which differs from parent material by a particular powdery structure (Russian Academy of Agricultural Sciences, 2008). The second order includes the soils which were formed under the influence of cryogenic processes and do not have a gleyic horizon, despite a perennial waterlogging. Thus, all other soils developed in permafrost-affected environments are attributed to other soil orders.

According to Bezuglova (2009) the new Russian soil classification, in spite of improvements in comparison with the soil classification system of 1977 (Tonkonogov et al, 2005), is still based the soil classification of 1977, and therefore has some limitations for the practical use. It was noted by Bockheim et al (2006) that the Russian soil classification system of 2004 does not have a taxon to reflect cryoturbation and permafrost occurrence in the soil. Some difficulties appear when permafrost-affected soils are described by Russian soil classification (Shishov, 2004). Lupachev & Gubin (2008) pointed out that a diagnostic horizon for permafrost-affected soils such as suprapermafrost gleyic horizon is not included to the Russian soil classification system.

Additionally, cryosol group does not include the organic horizons that are not developed at the soil surface (Lupachev & Gubin, 2012).

US Taxonomy

More than other soil classifications, the US soil taxonomy is considered to be soil survey-oriented. The structure of this taxonomy comprises the following levels: *order*, *suborder*, *great group*, *subgroup*, *family*, and *series*. Permafrost-affected soils occupy approximately 90 % of the Alaskan exposed land surface (Jones et al, 2010). In nomenclature, permafrost-affected soils were included only in the 8th edition of the US Soil taxonomy and defined as *Gelisols* (from Greek *gelid*, “very cold”) (Soil Survey Staff, 1998). The soils are considered to be *Gelisols* if they contain permafrost within 100 cm of the soil surface or gelic material within 100 cm of the soil surface and permafrost within 200 cm of the soil surface where the frozen layers comprise ice lenses, vien ice, segregated ice crystals, and ice wedges (Soil Survey Staff, 2010). One of the prerequisite for *Gelisols* is the occurrence of permafrost or soil temperature of 0 °C which does not reduce the characterization to a diagnostic soil horizon, like in the Russian soil classification, but to the occurrence of cold environment. However, Krasilnikov & Arnold (2009) and Tonkonogov et al (2009) emphasized that the distinction of this soil order by soil climatic condition criteria may result in a limitation of the significance of other soil-forming processes.

Canadian Soil Classification

The Canadian soil classification system was developed in accordance with geographical settings of the country and used the terminology and conceptions applicable for the local environment. The system has a hierarchical structure and consists of five categories: *order*, *great group*, *subgroups*, *family*, and *series* (Canadian Soil Classification Working Group, 1998). Permafrost-affected soils cover approximately 50 % of Canada (Jones et al, 2010). In the Canadian soil classification, permafrost-affected soils are described as *Cryosols*. They can be both mineral and organic and are characterized by features of cryogenic processes. The *Cryosols* order includes three great groups: Turbic *Cryosol*, Static *Cryosol*, and Organic *Cryosol*. The Canadian soil classification system is not based directly on soil genesis as in case of the Russian Soil classification but on soil-forming processes. Many soil scientists noticed certain similarities of the Canadian Soil Classification with the US Soil Taxonomy (e.g. Buol et al, 2003; Tarnocai & Bockheim, 2011). In both systems permafrost occurrence is recognized as the major factor,

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which drives the cryogenic processes and therefore, permafrost-affected soils development. Close correlation was also found between the great groups of Cryosols of the Canadian Soil Classification and suborders of Gelisols of the US Soil Taxonomy (Soil Survey Staff, 2010). This classification has fewer similarities with the World Reference Base for Soil Resources (WRB) soil groups (Tarnocai & Bockheim, 2011).

WRB soil classification

The World Reference Base for Soil Resources (WRB) soil classification system was developed by two international groups which originated from the World Soil Map legend and an International Reference Base. The system of WRB classification was developed in order to bridge all national classifications from across the globe. Additionally, it was aimed to be used as a base for the global soil resources assessment (FAO, 2006). In 2007, the WRB soil classification was translated into Russian (Targul'yan & Gerasimova, 2007) prompting many Russian soil scientists to acquaint oneself with the soil classification system and discuss advantages and disadvantages of other existent soil classifications (Tonkonogov, 2008). The WRB soil classification has a pronounced hierarchical structure which comprises two levels of the classification system: (1) reviewing soil groups and (2) compositions of the reviewing soil groups with qualifiers - prefixes and suffixes. This hierarchical structure is similar to the structure of the new Russian soil classification despite the critical distinction in the concept of soil as a subject of studies and the determination of diagnostic horizons between these soil classification systems (Tonkonogov et al, 2008). According to the WRB soil classification permafrost-affected soils are identified as Cryosols where the diagnostic cryic horizon (from Greek *kryos* - cold, ice) is described as a perennially frozen soil horizon in mineral or organic materials. The diagnostic criteria of permafrost-affected soils are similar to the criteria proposed for the US soil taxonomy (Soil Survey Staff, 2010). This fact makes easier to compare the studies of permafrost-affected soils to each other where the international and national approaches were used to define a soil taxa.

2.2.4.1 Correlation of soil classification systems

Many studies have been dedicated to correlating the different soil classification systems (e.g. Rozanov, 1974; Stolbovoy, 2000; Krasilnikov & Arnold, 2009; Jones et al, 2010). The importance of the correlation of soil units provided by different classification systems was

mentioned by [Gerasimova et al \(2009\)](#). In particular, further development of soil database and soil mapping should provide a key for the soil information exchange between the scientists. Some studies of permafrost-affected soils provided a correlation between soil names of Canadian soil classification and the US soil classification (e.g. [Smith et al, 1995](#)), and the Russian soil classification and the WRB soil classification (e.g. [Pastukhov & Kaverin, 2013](#)). Cryoturbation of soil material is used as a diagnostic criteria in classification systems including the soil taxonomy of Russian soil classification ([Shishov et al, 2004](#)), the US soil taxonomy ([Soil Survey Staff, 2010](#)), the Canadian soil classification ([Canadian Soil Classification Working Group, 1998](#)), and the World Reference Base for Soil Resources (WRB) ([FAO, 2006](#)). However, the factor of permafrost occurrence is disregarded only in the Russian soil classification. The different soil classification systems are based on different methodological approaches and therefore, the correlation between them may lead to controversial results.

Besides two correlation methods (pedogenic and substantive), [Gerasimova et al \(2009\)](#) suggested the cartographic method, i.e. overlapping of maps created by different soil classifications as a further approach in correlating the soil classifications. Figure 8 shows the mapping of the highest taxonomic units determined in three national soil classifications (Russian, American, and Canadian) and the international soil classification (WRB). It is immediately visible that Russian Cryozems appear to correlate well with American Gelisols, Canadian Cryosolic soils, and Cryosols of the WRB soil classification. However, these maps cannot fully depict the diversity of permafrost-affected soils. The contradictions in correlation of soils arise on a local scale. The results of these contradictions are shown using the example of the delineation of permafrost-affected soil types classified according to the US Soil Taxonomy (top) and Russian soil classification (bottom) (Fig. 9). Because soil classification and soil mapping are intended for different purposes, the result of these approaches is different. The taxonomic system classifies the soils as a single class everywhere, whereas the soil mapping distinguishes several classes of soils ([Stolbovoy, 2000](#)).

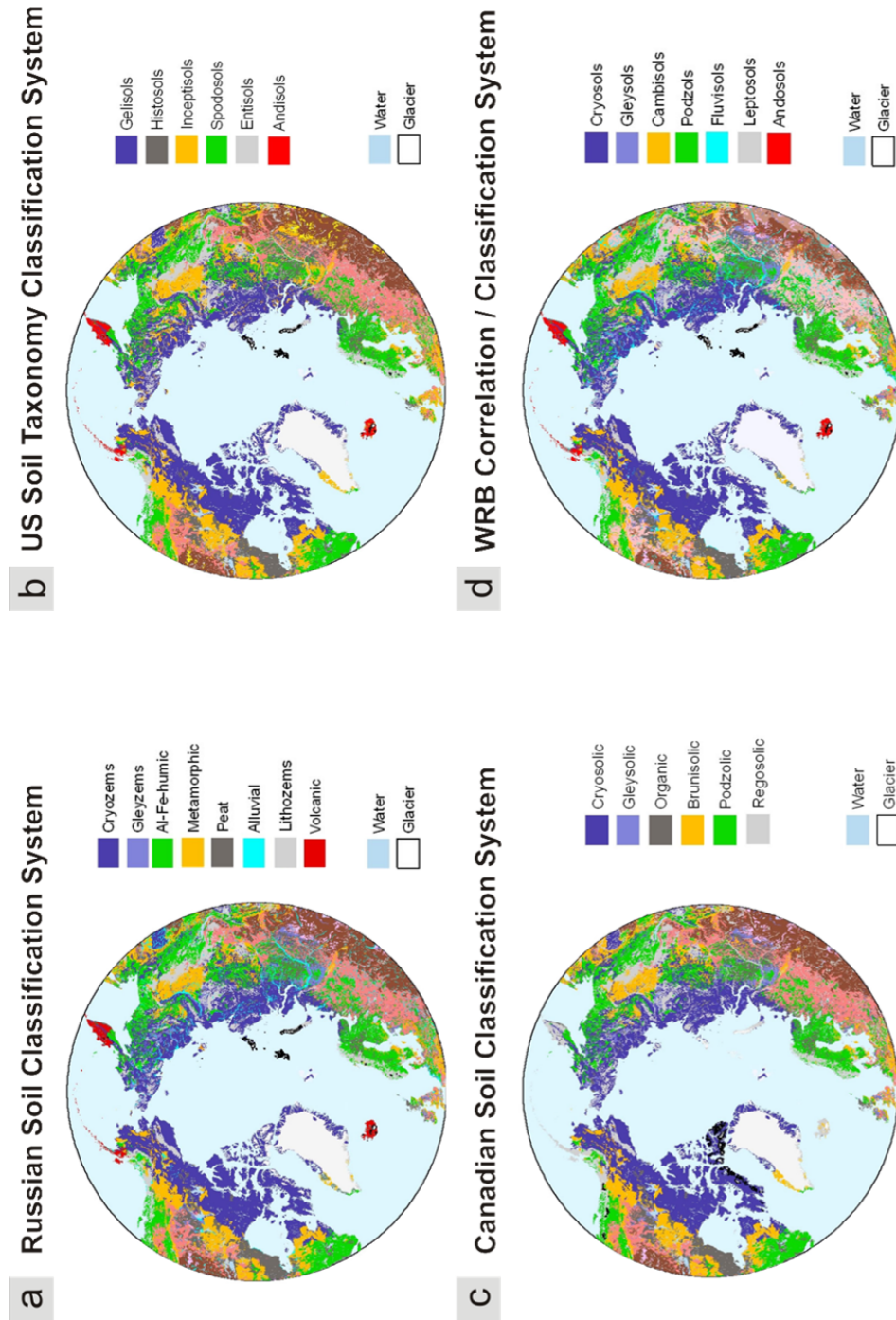


Figure 8: Maps of soil classification systems representing the major soil types of the Northern Circumpolar Region: (a) – Russian soil Classification system, (b) – US Soil Taxonomy, (c) – Canadian Soil Classification, and (d) – WRB soil Correlation/Classification by the “Cryosol Working Group” of the international Union of Soil Science. (European Commission – Joint Research Centre, European Soil portal – [Soil Data and Information Systems \(2013\)](#)).

As it was shown, difficulties of correlation of soil classification systems are primarily related to differences in methods applied to classify permafrost-affected soils. These differences may lead to incongruence in soil type landscape distribution (Gerasimova, 2007; Jones et al, 2010). Besides the different approaches used in classification of permafrost-affected soils, the complexity of soil correlation is embodied in the dynamic development of national and international soil classifications (Samofalova, 2013). Some studies suggested the use of certain soil criteria common for various soil classifications as a base for the comprehensive and effective classification delineation of permafrost-affected soils (e.g. Everett & Brown, 1982; Smith et al, 1995). Each group of soil classification systems developed the key to soils, in order to simplify the processes of soil classification working in the field, (FAO, 2006; Russian Academy of Agricultural Sciences, 2008; Soil Survey Staff, 2010).

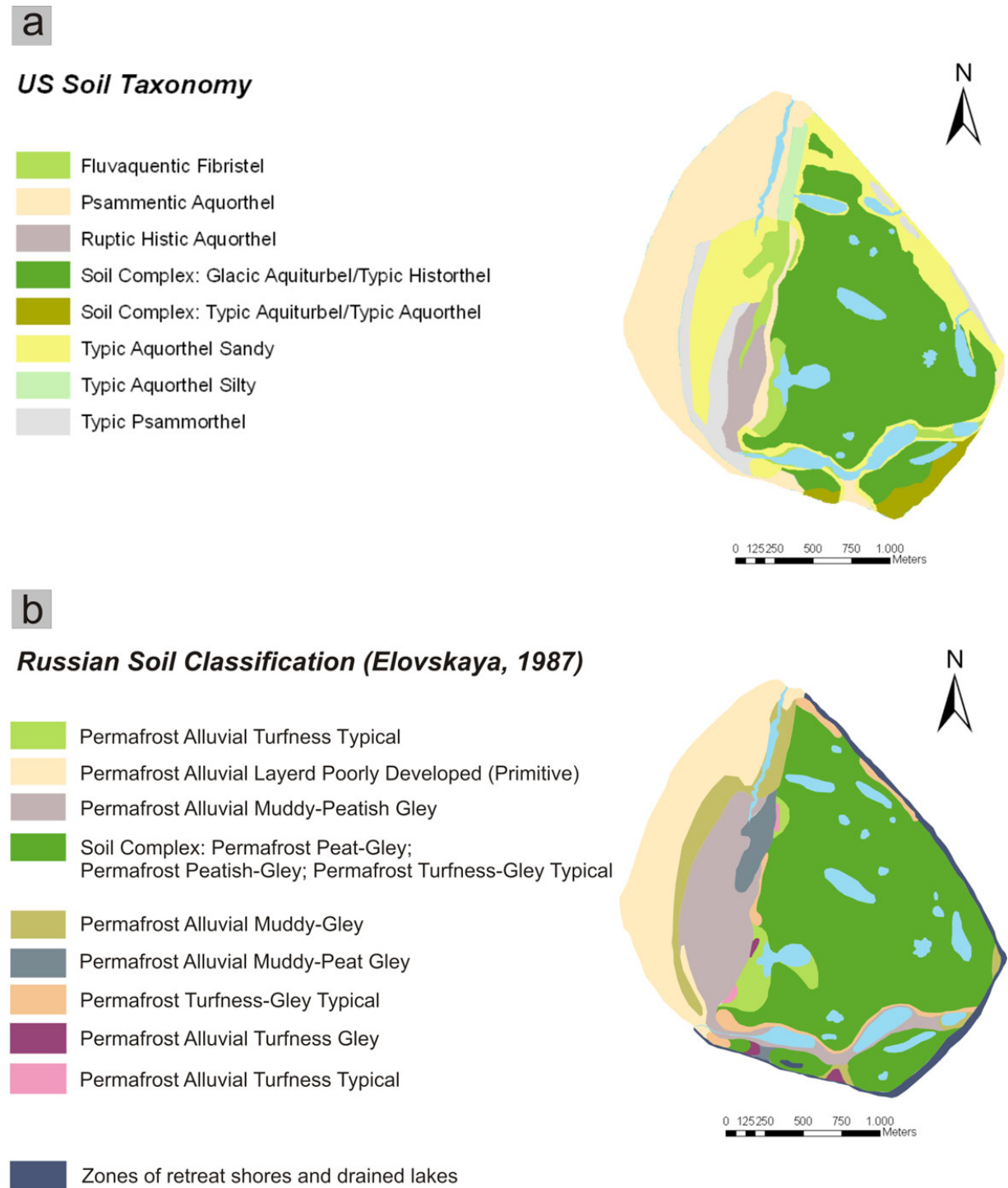


Figure 9: Soil units of permafrost-affected soils on Samoylov Island (Lena River Delta, northern Siberia). Soils described according to: (a) – the US Soil Taxonomy (Soil Survey Staff, 2010) and (b) – Russian Soil Classification (Elovskaya, 1987). Data taken from Pfeiffer et al (2000), Pfeiffer et al (2002), and Yakshina (1999a).

3. Investigation area

The investigation area is located in the northern part of the Yakutia region (Republic of Sakha) between 73.5° N and 69.5° N (Fig. 10). It covers the delta of the Lena River in the north and its nearby hinterland to the south which belongs to the Lena River drainage basin. The area belongs to a continuous permafrost region with permafrost depths ranging from 500–600 m and deeper (Gvozdetsky & Mikhaylov, 1978; Makunina, 1985; Zhang et al, 1999).

The study area belongs to the arctic-subarctic climate zone with continental and severely continental type climate. The continentality of climate is more evident going inland. It depends not only on domination of continental air mass and their circulation characteristics in this area but also on distance from the Arctic Ocean and mountain groups on the side of the Pacific Ocean (Makunina, 1985). This area of northern Siberia experiences a monsoonal change in wind direction (Sechrist et al, 1989). During winter period an intense, semi-permanent, cold Siberian High anticyclone is dominant. The regional particularities of the wind distribution occur over the investigation area. The prevailing winds are of south-western (inland section) and south-eastern (deltaic section) directions, being strongest over the coast and light or calm in the interior part of the area. During summer the central Lena Delta region undergoes varying weather fluctuations due to the change between the advection of cold and moist air masses from the Arctic Ocean, and warm and dry air masses from the Siberian mainland (Kutzbach et al, 2007). At this period winds of south-eastern, eastern, and north-western directions are prevailing. As it was shown by Ivanov et al (2009) the dominant winds in the Tiksi area, which is around 110 km away from the central part of the Lena River Delta (Samoylov Island), have southern, south-western, and western directions in the cold period whereas in the warm period the winds of northern and north-eastern direction are dominant. During the cold period strong winds could be observed only for dominant directions. In the warm period the strong winds come from almost all directions.

The region is generally characterized by high annual air temperatures amplitudes of warm and cold seasons, and low and unequal precipitation distribution during and among years. The topographic features have a great influence on all local climatic elements of the study area. The analysis of the archive meteorological data (Russian's Weather Center, 2013) also showed that temperature and precipitation amplitudes increase from the deltaic area in the north to the land area southward. Thus, the mean annual air temperature measured during the period 1998-2012 at

Chapter 3. Investigation Area

the climate station Dunai ($71^{\circ} 56' N$, $124^{\circ} 30' E$) was $-14.6^{\circ} C$, $-12.6^{\circ} C$ at the station Stolb Island ($72^{\circ} 24' N$, $126^{\circ} 21' E$), $-12.5^{\circ} C$ at the station Tiksi ($71.6^{\circ} N$, $128.9^{\circ} E$) was, and $-11.5^{\circ} C$ at the southernmost station Dzhardzhan ($68^{\circ} 49' N$, $123^{\circ} 59' E$). The mean precipitation measured at the Dunai northernmost station during the period of 2000-2004 was 228 mm, whereas at the climate reference site in Dzhardzhan the annual precipitation was 330 mm measured during the same period (Fig. 11).

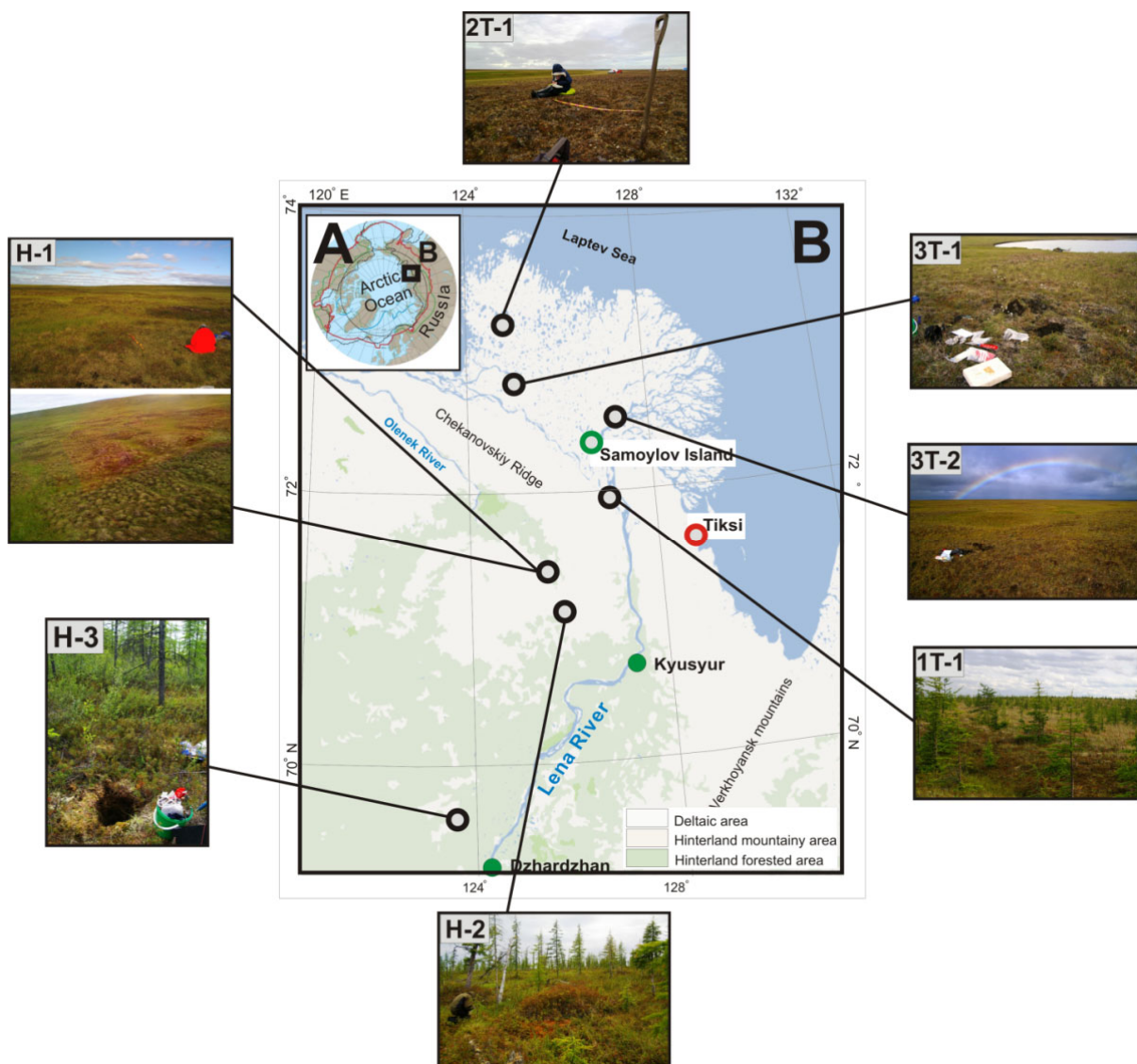


Figure 10: An overview map of study site locations. The studied sites 1T, 2T, and 3T belong to the first, second, and third Lena River Delta terrace, respectively. The studied sites “H” belong to the hinterland. Photos of representative landscapes are provided by S. Zubrzycki (Zubrzycki et al, 2012).

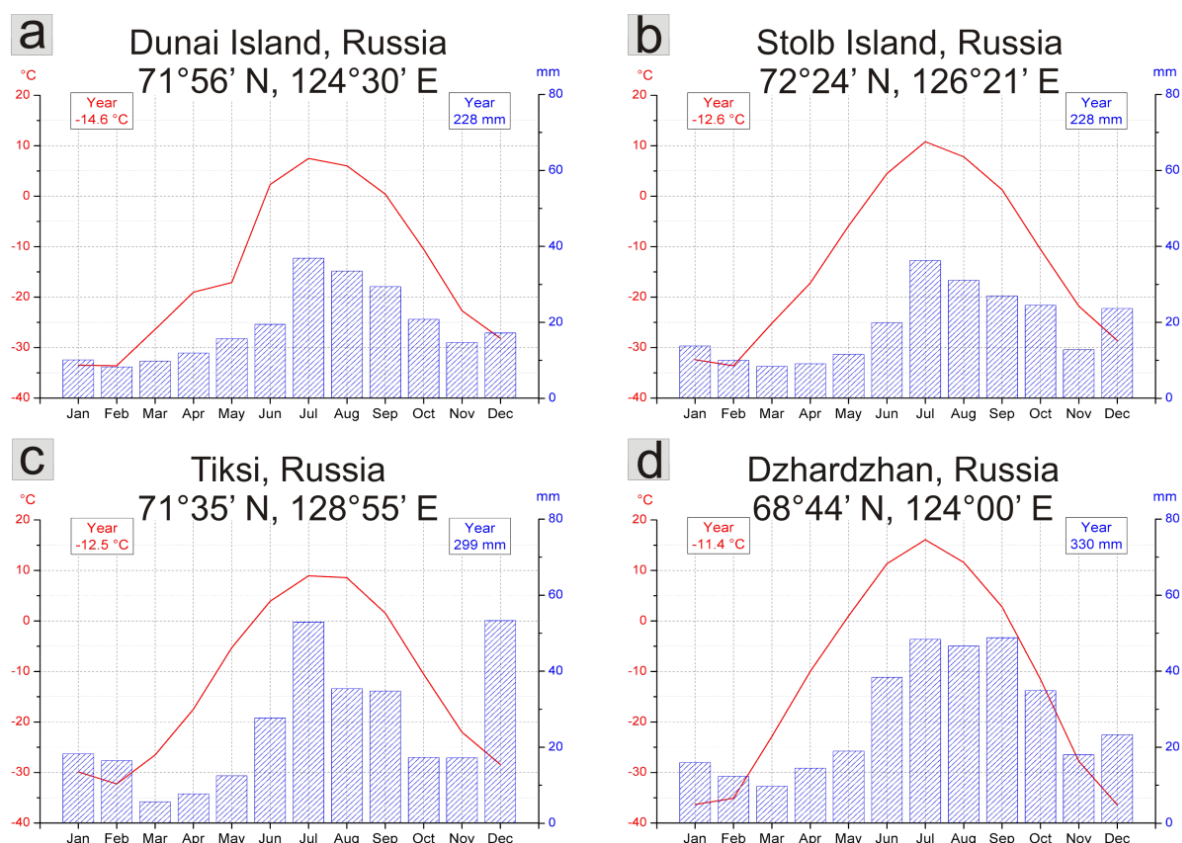


Figure 11: Mean annual temperature and mean annual precipitations observed at the stations: (a) – Dunai, (b) – Stolb, (c) – Tiksi, and (d) – Dzhardzhan during the period 1998 – 2012 for temperature data and 2000 – 2004 for precipitation data, respectively. Data are provided by [Roshydromet \(2011\)](#) and [Russian’s Weather Center \(2013\)](#).

Over the whole study area the winter period lasts 6-7 months. Polar night lasts from November to January. The snowmelt typically starts in the beginning of June and the growing season lasts from the middle of June to the middle of September. Polar day lasts from May to the beginning of August. The summer period is short with drizzling rain and sometimes with snow in the north ([Isachenko, 1985](#)). About 45% of the precipitation falls as rain during the growing season. Because of a strong continental climate in the study area, the summer period is longer and warmer in the south regions. [Luybomirov \(2005\)](#) noted that accumulated summer air temperatures can vary from 4-5 °C in the north to 25-40 °C in the south of the northern Yakutia region. However, accumulated winter temperature isotherms are not governed by the same trend.

3.1 Study sites of the Lena River Delta Region and its Hinterland

The Lena River Delta has an area of around 28.000 km² and is situated on the shallow Laptev Sea shelf. The plain was formed down to the water gap between Chekanovkiy and Tuara-Sise Ridges (Makunina, 1985). The delta falls into islands by 880 channels which are mottled with an abundance of thermokarst lakes. The Lena River is one of the largest rivers in the Arctic that flows northward from mid-latitudes to the Arctic Ocean. The drainage area of the Lena River basin is 2.430.000 km² and it contributes about 15% of total freshwater flow into the Arctic Ocean (Yang et al, 2002). The river carries from 15×10⁶ to 21×10⁶ tons of suspended sediments out to the delta per year (Makunina, 1985; Gordeev & Sidorov, 1993; Yang et al, 2002). The Lena River has a very low winter flow and a very high peak flow in June, about 55 times greater than the minimum discharge. The interannual variation of the Lena River monthly discharge is generally smaller in the cold season and larger in summer months mainly due to floods associated with snowmelt and rainfall storm events (Yang et al, 2002).

The ID names, location, and landscape description of the studied sites of the Lena River Delta are shown in Appendix (Tab. I). According to Grigoriev (1993), the Lena River Delta area can be subdivided into three terraces of various floodplain levels and different ages. The highest third terrace (30 – 55 m a.s.l.) was formed during the late Pleistocene and is exposed in the western and fragmentarily in the southern part of the delta (Schirrneister et al, 2003). The deposits of that terrace consist of so-called Ice Complex enhanced by peat and sand accumulations overlying sequences of sandy sediments with a high content of segregated ice (Strauss et al, 2012). This geomorphological unit is represented by the Khardang-Sise Island in the west (site 3T-1) and the Sardakh Island (site 3T-2) in the south-east of the Lena River Delta. Being located at the southern part of the Trofimovskaya channel, Sardach Island was considered to be a relic part of the third terrace of the Lena River Delta. This unit is characterized by typical polygonal sedge-moss tundra with the dominant species *Carex sp.*, *Dryas punctata*, and *Poaceae* family in herbs layer that occupies up to 60 % of the total vegetation coverage. The moss cover reaches 90%. The study site of Khardang-Sise was located at the eastern part of the island sidewise the Olenekskaya channel. Topographically the area around was composed of relatively smooth surface plains 800 m south-west from the Mutnoe Lake. The moss layer was dominant and amounted to 90 % of total vegetation cover. The herbs layer consisted mainly of *Dryas punctata* and *Poaceae* family species and contributed up to 50 % of the foliage cover.

Arga Island (site 2T-1) is the northernmost site of the study area. It is located in the north-western part of the Lena River Delta and represents a major part of the second terrace (20 - 30 m a.s.l.) of the delta (Schwamborn et al, 2002). This unit is characterized by coarse-grained sandy sediments, which were formed from the late Pleistocene to late Holocene (Schwamborn et al, 2002; Kuzmina et al, 2003; Wagner et al, 2007). The vegetation of the studied site comprised mosses covering 90 % and herbs with the dominant species *Carex sp*, *Cassiope tetragona*, and *Luzula sp* occupying 30 % of the total vegetation cover.

The first terrace including active floodplains (1-12 m a.s.l.) formed during the early Holocene and covers the main part of the eastern delta sector between the Tumatskaya and the Bykovskaya channels (Schwamborn et al, 2002). It is assumed to represent the “active” delta within the study locations on Samoylov Island (72° 22' N, 126° 31' E) and on Tit-Ary Island (site 1T-1) which is situated in the main Lena River channel south-east of Samoylov. Polygonal tundra is typical for the landscape units on both islands and is characterized by two different forms: polygon centres that are water saturated and contain a large amount of organic matter due to accumulation under anaerobic conditions, and polygon rims that show evidence of cryoturbation in more or less all horizons of the active layer. The polygon rims show a distinctly lower water table and less accumulation of organic matter (Pfeiffer et al, 2002; Fiedler et al, 2004; Kutzbach et al, 2004). The Tit-Ary Island belongs to the northernmost places of tree-limit in the Russian Arctic. The canopy layer at the studied site was sparsely distributed and occupied around 5 % of the total vegetation coverage. The moss layer played a dominant role in forming the sparse forest floor and amounted to 80 % of the total vegetation coverage. Shrubs comprising *Ledum Palustre* (H.) and *Betula nana* (L.), and herbs with the dominant species *Carex sp*, *Eriophorum medium* (Andersson), *Luzula sp*, *Pedicularis sp*. contributed 70 % and 30 % to the total vegetation cover, respectively. The studied units of Samoylov Island are described in details in the following subsection below.

The region of the north slope of Chekanovkiy Ridge represents a transitional zone between the Lena River Delta and the Siberian mainland. The investigation sites of the nearby hinterland were located on the slopes of the Chekanovskiy Ridge on the western side of the Lena River (Fig. 10). In regard to lithological structure the sites of the hinterland represented the eastern margin of the Siberian platform westward the Lena River. The studied sites falling within the Central Siberian Plateau represented patches of pronounced visible changes in vegetation cover.

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According to [Isachenko \(2002\)](#) this region pertains to Sub-Arctic southern tundra landscapes, low land forest tundra Siberian landscapes, and partially to northern taiga east-Siberian boreal landscapes further to the south. The site H-1 (71° 10' 26.29" N, 124° 34' 29.80" E) representing southern tundra was situated on a relatively flat plain with an elevation of 160 m a.s.l., 50 m north to the El'gene-Kuele Lake. It was characterized by smaller percentage of moss coverage (up to 50 %) in comparison with a typical tundra zone, but predominant by herbs and shrubs (up to 60 %) among which were the species *Betula nana* and *Ledum Palustre*.

The site H-2 (70° 55' 22.76" N, 125° 33' 3.13" E) belonged to the forest tundra zone. This forested area had sparsely distributed species of *Larix Sibirica* (*Ledeb.*). As a “drunk” forest area, it was characterized by a slightly inclined landscape with small-size elevated hills which developed due to heaving processes. This site was dominated by moss species covering up to 100 % of the area. The coverage by shrubs and herbs amounted to 60 % and 20 %, respectively.

The site H-3 (69° 23' 56.83" N, 123° 49' 33.96" E) was the southernmost unit of the pilot study. It belonged to the northern taiga vegetation zone and was located around 100 m south-west to the Sysy-Kuel' Lake. The vegetation diversity in the tree layer comprised 5 to 7 m height *Larix Sibirica* and was characterized by relatively high tree coverage (up to 50 %). The foliage cover by herbs was small and amounted to 1% of the total vegetation coverage, whereas shrubs with dominant species *Betula nana*, and *Alnus crispa* composed up to 70 % of the coverage.

Samoylov Island

The investigations of the soils were mainly carried out on Samoylov Island in the southern-central Lena River Delta (Fig. 10). Since 1998 the research station has been functioning on Samoylov Island and serving as the base for multi-disciplinary studies ([Hubberten et al, 2006](#); [Grigoriev & Hubberten, 2012](#); [Bolshiyarov et al, 2013](#)). The geomorphology of the island was studied in detail in previous years ([Boike et al, 2013](#); [Bolshiyarov et al, 2013](#)). This site is representative of the younger delta areas including a Holocene estuarine terrace and various flood-plain levels (Fig. 12). The western part of the island represents the floodplain (site middle floodplain MF-1). Frequent changes of the river water level create different periods of sedimentation and result in the formation of stratified soils and sediment layers which are dominated either by mineral substrates with allochthonous organic matter or pure autochthonous peat ([Boike et al, 2013](#)). The site MF-1 (72° 22' 51.61" N, 126° 28' 28.37" E) was chosen as

representative for this part of the island. It was located on a gently inclined floodplain at an elevation of 3 m a.s.l. The vegetation coverage comprised mainly *Poaceae* family species (*Dischampsia caespitosa* L. and *Arctophilla fulva*) and amounted to 60 %. Presence of moss species was estimated to be no more than 2 % of the total vegetation cover.

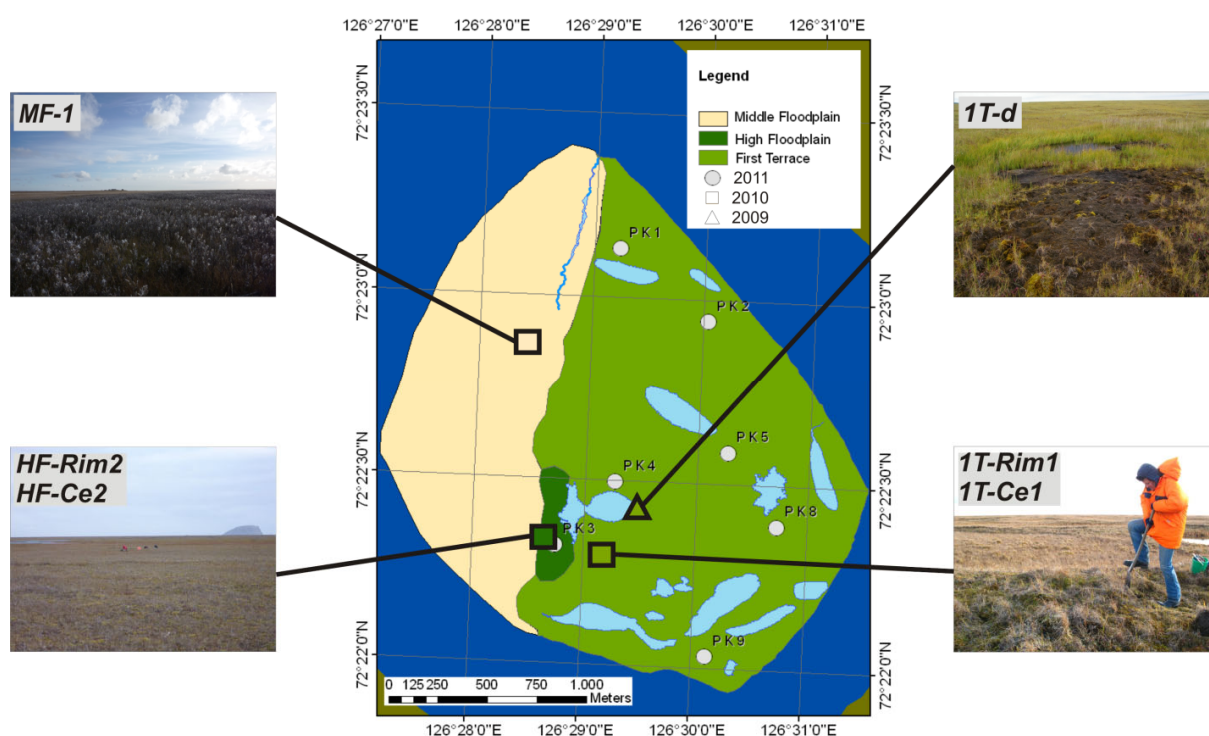


Figure 12: A map of Samoylov Island showing: (a) – geomorphological units of the island (shown by colours) and (b) – location of site investigated during field expeditions in 2009 (denoted by a triangle sign), 2010 (denoted by a quadrature sign), and 2011 (denoted by a circle sign). Own photos of the investigated sites (2010).

The high flood-plain is fragmentarily situated between the east coast of the island and the western border of the estuarine terrace above the middle floodplain. This area could be described as a thermokarst depression of the terrace above the floodplain, because it is composed of the same layered plant detritus-sand deposits of the ancient delta floodplain. It is inundated only during exceptional annual floods (Akhmadeeva et al, 1999; Kutzbach, 2006). The sites HF-Rim2 and HF-Ce2 belonged to polygon rim and polygon centre, respectively. These two micro relief forms developed a polygon of a hexagonal form with slightly pronounced edges. The vegetation of the polygon rim was dominated by *Salix sp.*, *Arctagrostis sp.* with hummocks of

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Arctostaphylos Alpina (L.). The coverage of mosses was prevailing and amounted to up to 97 %. Even with a small elevation gradient between two forms of relief, the difference in vegetation cover was expressed by a dominance of hygrophilous *Carex* species in the polygon centre site.

In contrast to the accumulative floodplain site, erosion processes dominate the eastern shores of the island and form an abrasion coast. This part is represented by an ancient estuarine (river-marine) terrace, which covers about 70% of the total area of the island (Akhmadeeva et al, 1999). The sites 1T-Rim1 and 1T-Ce1 represented two micro relief forms - a notably elevated polygon rim and water saturated polygon centre, respectively. The polygon rim was characterized by presence of moss and lichen species (cvg. 90 %). The coverage of herbs was dominated by *Carex aquatilis*, *Dryas octopetata* (Linn.), *Pedicularis lapponica* (L.), scattered *Luzula* sp. and *Arctagrostis* sp. The polygon centre was composed of an abundance of small hummocks comprising *Carex aquatilis* (Wahlenb.) species and covered by mosses 100 %. On the skirts of the centre *Eriophorum* species and shrubs (*Salix reticulata* (L.)) were dominant among others. The additional site with the name ID 1T-d represented hummocky microrelief forms of the ancient estuarine terrace near the Fish Lake. At that small site a diesel generator which supplied the micro-meteorological eddy covariance measurement system was located. After demounting the diesel generator together with the measuring system, the vegetation and soil cover of this site were disturbed by diesel fuel spill.

3.2 Tiksi area and investigated sites

The area of Tiksi is located between the Lena River and the Kharaulach River mouths. It covers parts of Primorsky Ridge and Kharaulach Mountains which is a part of the Verkhoyansk Range. The area belongs to the Verkhoyano-Kolymanorogenic system of Mesozoic time. Its bedrock was formed by disturbed Palaeozoic terrigenous rocks and composed of hard Permian aleurolites, mudstones, and sandstones, and much softer Carboniferous sandstones, mudstones, and shales, all striking north-south (Grosswald et al, 1992). The deeply eroded surface of Palaeozoic is covered by deposits of a Cenozoic complex which formed intermontane troughs. The lowest stratum of these formations is composed of sands and clays of Paleocene and Eocene age. More unconsolidated sediments of Oligocene and Miocene age cover these deposits which were found out also in the Lena Delta on the Sardahk Island. The younger stratum belongs to the Pliocene-Quaternary period. It is composed of gravels, sands and aleurites together with peat

material. The youngest geological layer is composed of unconsolidated sediments of Pleistocene and Holocene age (Grosswald & Spektor, 1993).

The observation sites were investigated across the area in the immediate vicinity and at a distance to Tiksi settlement to get a first idea about the geochemical composition of permafrost-affected soils and to evaluate possible anthropogenic influences on the surrounding area of the settlement. The remote sites were situated very close to the Lake Sevastian which is the largest reservoir of the Tiksi area. It is located 10 km south of the Tiksi settlement. The landscapes which are located west to the lake comprised of sandstones of the Permian period whereas the eastern part of this area and the lake margins were formed by soft shales of the Tiksian suite (Grosswald & Spektor, 1993).

Figure 13 shows an overview map with locations of 15 investigated sites with ID index “TH”. North of Tiksi, the investigations of four sites TH9, TH10, TH11, and TH14 were carried out (referred as northern sites). The unit TH9 was located on a slightly sloping plain in front of the Bulunkan Gulf 50 m from the road to the “Tiksi” airport in the west and 150 m from the power transmission line in the east. The investigation sites TH10 and TH11 were located on typical tundra polygon landscape near the Melkoe Lake. The study site TH14 was located next to the Bulunkan Gulf, on the inundated area 35 m from the water level. This micro relief was composed of narrow cracks and an abundance of hummocks. A small transect composed of three observation points TH3, TH4, and TH5 in the south-western direction from the Tiksi settlement (referred as western sites) was located on the slope southward Stolovaya Mountain, parallel to a winter road, downslope to the innominate lake north-north-eastward to the Diring Kuel’ Lake. The land presented a slightly developed polygon structured landscape. The studied sites TH8, TH12, and TH13 (referred as eastern sites) were situated on the eastern and north-eastern slopes of Lel’kina Mountain, 800 m south-west from a petroleum storage depot. They represented a hummocky tundra plain inclined sideward the Tiksi bay. The site TH15 belonged to a low-lying waterlogged land north-west to the Lel’kina Mountain. The remote sites TH1, TH2, TH6, and TH7 (referred as southern sites) were located 8-10 km south from the Tiksi settlement, alongside the Kopchik-Yuryage River which runs into the Sogo Gulf. The sites TH6 and TH7 were situated in immediate proximity to the Sevastian Lake. The area comprised typical moss-lichen tundra with poorly developed polygons (Appendix, Tab. II). The relief changed often to fenlands and patchy to elevated areas with aleuroite sediment exposures.

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The study area belongs to the zone of the East Siberian sub-Arctic tundra. In this environment, grasses and mosses contribute to the modern vegetation (Andreev et al, 1987). Moss coverage for all studied sites, except for TH9 and TH14, amounted to 70 to 90 % of the total vegetation coverage. The dominant species *Carex sp*, *Eriophorum sp*, and *Salix sp*. were found at the sites TH1, TH5, TH6, and TH15, that belong to depression microrelief forms. The sites TH7, TH11, and TH14 are located on an elevated part of a plain and were characterized by dominance of *Carex sp*, *Salix sp*, *Polygonum sp*, and *Poaceae* family species. The rest of the investigated sites belong to a sloping plain micro morphological unit. The dominant plants *Carex sp*, *Cassiope tetragona (D.Don)*, *Dryas sp*, *Betula nana (L.)*, *Vaccinium vitis-idaea (L.)*, and *Pedicularis sp* were found.

The settlement Tiksi (71° 38' 12.61'' N, 128° 52' 04.56'' E) is located on the coast of the same-named bay in the Laptev Sea to the south-east from the Lena River mouth. From the opposite site of the bay the settlement is surrounded by several moderately high mountains from 200 to 300 m height. Tiksi is the administrative centre of the Bulunsky district of the Sakha Republic (Yakutia). It was founded in 1933 as one of the stations of the Northern Sea Route. One of the northernmost maritime ports is located on the western coast of the Laptev Sea in close vicinity to the village. The port is specialized on transport of food and architectonic cargo, coal, round timber, and petroleum items. Because of adverse climatic conditions navigation lasts for only 90 days per year. The polar meteorological station "Polyarka" (Fig. 13) founded in 1932 and the polar geocosmic observatory "Tiksi" founded in 1957 are located 7 km south of Tiksi. The Tiksi Airport of federal significance is located 7 km to the north of the settlement. The population of the settlement has substantially decreased over the last years. A considerable amount of abandoned houses was observed in the settlement. A vast household waste deposit was located several kilometres west of Tiksi near the foot slope of Stolovaya (Stollakch-Khaya) Mountain (319 m a.e.l.) (Fig. 14a). The settlement area and its neighbourhood were also characterized by considerable littering of old steel, fuel tanks, and rubbish (Fig. 14b). An old stone-pit was located approximately 600 m south from Melkoe Lake (Fig.13 and 14c).

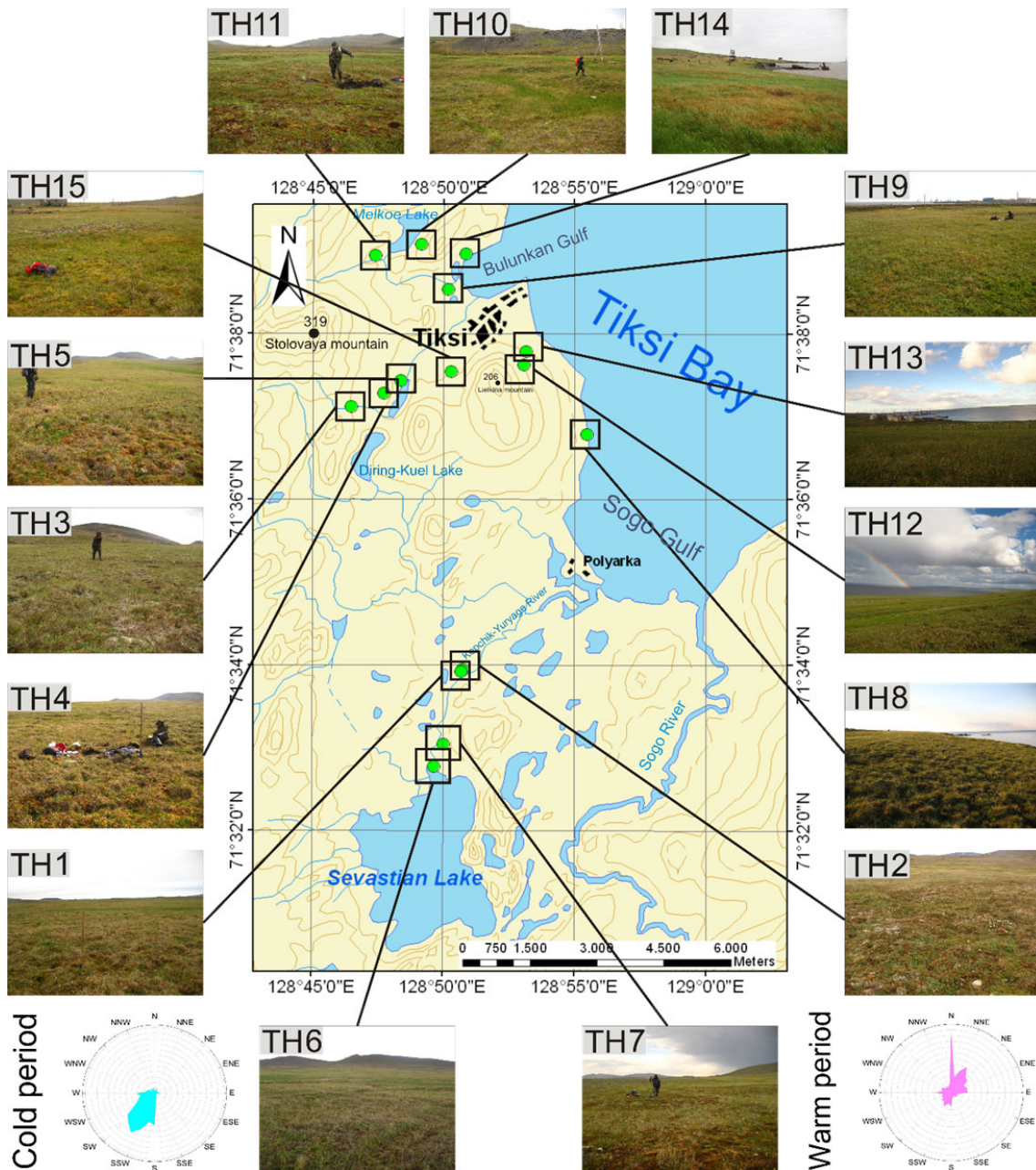


Figure 13: An overview map of investigation sites of the Tiksi area. Remote sites are represented by TH1, TH2, TH6, and TH7; Western sites are represented by TH3, TH4, and TH5; Eastern sites are represented by TH8, TH12, TH13, and TH15; Northern sites are represented by TH9, TH10, TH11, and TH14. The diagrams in the bottom of the figure represent the long-term average monthly wind rose for the cold period (September - February) with prevailing winds of southern, south-western directions and the warm period (March-August) with prevailing winds of northern and north-eastern directions, respectively. Based on the data provided by [Russia's Weather Server \(2013\)](#) for the period of 1998 – 2012. Own photos of representative landscapes (2011).



Figure 14: General view of: (a) – a waste landfill on the downslope of the Stolovaya Mountain, (b) – old fuel tanks found on an exposed district and a road-side in immediate vicinity of the town Tiksi, and (c) – an old stone-pit. Own photos (2011).

4. Materials and methods

4.1 Field investigations

Field investigations were carried out in Northern Siberia in 2009-2011 covering the Lena River Delta region, its hinterland, and an area near settlement of Tiksi. Detailed description of the investigation area is performed in the Section 2.2.4.

4.1.1 Soil survey

During field work representative sites for each unit of the study area were chosen. Macro- and micro-relief forms, vegetation cover with dominant species, and visible anthropogenic changes were described. Each horizon of the investigated soil profiles was characterized using the following parameters: soils depth, soil colour, texture shape and size, humus content, decomposition stage of organic matter, inclusions, and root penetration (AG Boden, 2005). The soil order and soil type were determined for each soil profile using the Russian soil classification (Elovskaya, 1987), US soil taxonomy (Soil Survey Staff, 2010), and the results are presented in the Section 5.

Soil samples were collected in autonomous (elevated areas), transit (slopes), and accumulative (depressions) forms of a (micro)-relief. This approach allowed the observation of migration and accumulation processes of trace elements in the studied landscapes. The samples were taken from each genetic soil horizon within the active layer. On Samoylov Island, soils samples were collected also cm-wise in order to determine features of the vertical element distribution within the profile. Additionally, mixed top soil samples were collected from polygon rim sites (5 subsamples from one polygon) to detect possible metal atmospheric transport of trace metals. The collected samples were stored in plastic bags, and analysed at the Institute of Soil Science (University of Hamburg, Germany).

4.1.2 Vegetation survey

One of the most easy-to-use and informative methods of environmental assessment is bioindication. This method is based on the analysis of the chemical composition of indicator

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species and helps to determine the features of translocation and transformation of pollutants in environmental components. An adequate choice of indicator species plays an important role in the method's efficiency. Therefore, they must meet several requirements as: (1) a vast geographical distribution, (2) a possibility to assess environmental pollution in a very short time, and (3) an explicit and quick reaction to contact with toxic substances (Dołęgowska et al, 2012).

Shrubs (*Vaccinium vitis-idaea* (L.)), mosses *Aulacomium* sp. and *Hylocomium splendens* (Hedwig.), and lichen *Cetraria cucullata* (Bellardi.) species were used in this study (Fig. 15), since they meet the requirements described above. Cowberry is a chimochlorous shrub of the *Vaccinium* genus. The species morphology is characterized by scleroid and leather-like leaves. In undisturbed environments, a cowberry species has an epidermic tissue with a thicker layer of scarfskin (cuticles) on the adorsal side of the leaf compared to underneath. A bloom wax covers the dorsal side of the leaf and probably limits the input of toxic gases decreasing harmful effect on the species. *Vaccinium vitis-idaea* species thrive on dry, moist, and strong swamped soils of different texture, on rocky hills, and sometimes on relatively well drained parts of bogs (Yudina, 1986). This species is capable to take up the available forms of some metals from the soil. However, high metal concentrations can cause not only morphological changes appearing in form of chloroses, but also internal damages to anatomic structure of the plant (Balaganskaya & Kudrjajtseva, 1998; Opekunova, 2004). Mosses and lichen species are often used as indicators of terrestrial ecosystem trace metal atmospheric pollution (Carlberg et al, 1983; Glooschenko & Arafat, 1988; Grodzinska & Godzik, 1991; Steinnes et al, 1992; Berg et al, 1995; Nash & Gries, 1995a; Nash & Gries, 1995b; France & Coquery, 1996; Berg & Steinnes, 1997; Minger & Krähenbühl, 1997; Fernández et al, 2000; Walker et al, 2006a; Walker et al, 2009; Aboal et al, 2010; Blagnyte & Paliulis, 2010; González-Miqueo et al, 2010; Harmens et al, 2010; Valeeva & Moskovchenko, 2011; Salo et al, 2012). Both mosses and lichens have no root system, so they take up essential elements directly from the air (Rühling & Tyler, 1970; Wolterbeek et al, 2003; Dołęgowska et al, 2012). The morphology of these species does not vary with seasons. This fact encourages an accumulation of pollutants throughout the year (Sloof, 1993). The cell walls of mosses can easily be penetrated by metal ions due to the lack of natural protective barriers, i.e. epidermis and cuticule. Porous structure of lichens formed due to a symbiosis of fungal and algal components also results in their capture of pollutants falling from the atmosphere (Klein & Vlasova, 1992). As in bryophytes, the uptake of metal ions by lichens occurs mainly or partly due to passive ion exchange (Tyler, 1989).

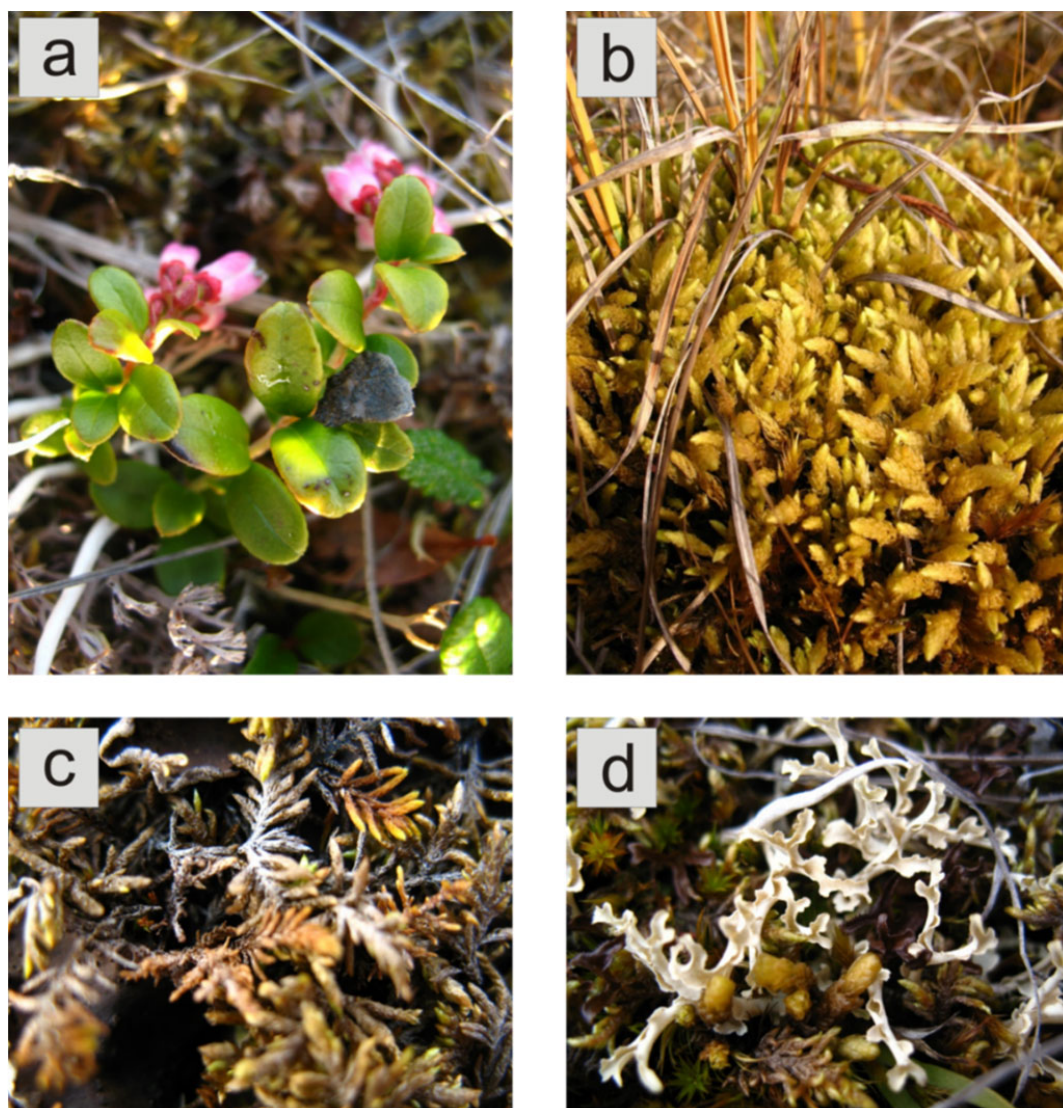


Figure 15: Individual plant species groups chosen as bioindicators of environmental state: (a) - *Vaccinium vitis-idaea* (L.), (b) - *Aulacomnium* sp., (c) - *Hylocomium splendens* (Hedwig.), and (d) - *Cetraria cucullata* (Bellardi.). Own photos (2011).

The vegetation survey was carried out during the summer of 2011. The vegetation coverage, the amount of species, and the morphological structure of indicator plant species (such as chlorosis) were determined on representative sites within an area of 10×10 m. At each representative site mosses (*Hylocomium* sp. and *Aulacomnium* sp.), lichens (*Cetraria cucullata*), and shrubs (*Vaccinium vitis-idaea*) were collected. For each species several sub-samples were taken and combined to one sample. The samples were dried at room temperature and kept in polyethylene bags in a dark case until analyses.

4.2 Laboratory analyses of physical and chemical properties of permafrost-affected soils

4.2.1 Sample preparation

Prior to analyses, all soil samples were air-dried to constant weight. All inclusions were removed from the soil matrix. The soil samples were passed through a 2 mm sieve and homogenized. Parts of the sieved fraction were grained to a powder using a tungsten-carbide-cartridge (Scheibenschwingmühle-TS, SIEBTECHNIK GmbH, Mülhheim an der Ruhr, Germany) in a vibration disk (1.5 min for mineral samples, and 30 sec for organic-rich samples), and were used for the determination of total carbon and nitrogen content, and trace metal content. Plant samples were first air-dried, than freed from inclusions, and cleaned from dust. The obtained material was chaffed, and grained to a powder using a tungsten-carbide-cartridge in a vibration disk for 30 sec. Ground soil and plant samples were dried in an oven at 105 °C and at 40 °C, respectively.

4.2.2 Soil texture analysis

The soil grain-size composition was determined using the [DIN ISO 11277](#) standard method. The dispersive state of soil material was detected by the proportions of various soil fractions and expressed as weight percentage. Prior to the analysis, soil samples which contain more than 2 % of organic carbon were treated with H₂O₂ (30 %) to avoid particle cementation with organic matter. For the soil texture determination, 30 g of dried soil material were mixed with 25 mL of sodium pyrophosphate Na₄P₂O₇ (0.4 M), to improve dispersion of particles, and 100 mL of distilled water. The samples were shaken for 18 h in an overhead shaker. The suspensions obtained were put into a glass cylinder and filled up to 1000 mL. The grain sizes of soils within the fractions less than 63 µm were analysed with a SEDIMAT 4-12 (UGT GmbH, Müncheberg, Germany). Before the analysis the samples were stirred, in order to obtain statistically well distributed suspensions in the water column. After predetermined intervals, aliquots of 10 mL were taken by an auto sampler, with depth and time being based on Stokes' law. To avoid adsorbing effects between glass and sample material, the aliquot was filled into a bromosilicate glass, dried at 105 °C, and weighted. Determination of the granulometric spectra in the fractions greater than 63 µm was carried out by dry screening method using sieves of 63, 125, 200, and

630 μm cell diameters, respectively. The obtained sample at each sieve size was weighted. The grain size distribution of the sample was calculated and given in %. Soil texture classes were given according to [AG Boden \(2005\)](#).

4.2.3 Water content

The soil water content is the mass of water in a soil expressed in per cent of the dry soil mass. The determination of the soil water content was carried out using the gravimetric method according to [DIN 18121-1](#). 10 g of a moist soil sample were weighted, dried at a temperature of 105 °C for 24 hours, and then weighted again. The soil water content of the sample was then calculated using equation 1.

$$\% H_2O = \left(\frac{\text{mass } H_2O}{\text{mass oven dry soil}} \right) * 100 \% \quad (\text{Eq. 1})$$

4.2.4 Organic matter content in soils and ash content in plants

The analysis of organic matter content of soil samples was carried out by the determination of weight loss during combustion in a muffle furnace at 550°C for 4-5 hours ([McKeague, 1978](#)). The organic matter content was calculated using equation 2, where *mass C* is the difference in mass before and after combustion, the so called loss on ignition (LOI). The accuracy of the method was 0.05 %.

$$\% C = \left(\frac{\text{mass } C}{\text{mass oven combusted soil}} \right) * 100 \% \quad (\text{Eq. 2})$$

Ash content in plant materials was determined by the same method. The substance remaining after this procedure is ash. Its content is presented in % of the mass oven-dried sample (equation 3).

$$\% C_{ash} = \left(\frac{\text{mass ash}}{\text{mass oven dried plant}} \right) * 100 \% \quad (\text{Eq. 3})$$

4.2.5 Soil pH

Soil reaction (pH) using H₂O and 0.01M CaCl₂ extracts was measured according to Bassler (1997) and DIN ISO 10390 by potentiometric method. Two soil suspensions with soil-water ratio 1:2.5 for soils with low organic carbon content, and ratio 1:25 for organic-rich soils were made. The obtained suspensions were stirred and after 1 hour of stirring measured with a pH-electrode (Type CG 820; Schott Geraete GmbH, Germany). The pH-meter was calibrated with standard buffer solutions of pH 7, pH 9, and pH4, prior to measurement.

4.2.6 Electrical conductivity

The electrical conductivity (EC) was detected in soil solutions according to DIN ISO 11265. To make the solution, 20 g air-dried fine-grained material (< 2 mm sieved) were mixed with 100 mL water (maximum conductivity 0.2 mS m⁻¹ at temperature 25 °C), and shaken for 30 min. In case of organic soils, 25 mL organic material was mixed with 75 mL water and stirred several times. After the extraction, the electrical conductivity in the obtained solutions was measured with a conductivity meter (Model WTW, LF 90, Germany).

4.2.7 Total carbon and nitrogen contents

The measurement of total carbon and nitrogen contents was based on gas chromatography using C/N analyser (Vario MAX CNS, Elementar Analysis System, Hanau, Germany). Fine-grained soil and plant material (600-800 mg of mineral samples, and 245-280 mg of organic-rich and plant samples) was combusted at 900 °C temperature (DIN ISO 10694). The released gases were dried and passed over a copper oxide catalyst where CO was oxidized to CO₂ and NO_x was reduced to N₂. Both CO₂ and N₂ were measured by thermal conductivity. The results of C/N analysis were given in % of the dry soil sample weight. Analytical error of this measurement was less than 0.5 %.

4.2.8 Cation exchange capacity (CEC)

The exchangeable cation contents were extracted with a 1M ammonium chloride solution according to [DIN EN ISO 11260](#). For the extraction procedure, 5 g air-dried fine-grained soil material and 25mL solution were mixed, shaken, centrifuged at 3000 rpm for 10 min, and the obtained supernatant was decanted in a 200 mL volumetric glass flask. These steps were repeated 3 times. After, the samples were mixed with 25 mL ammonium chloride solution, centrifuged, and stored for 24 hours. Later, the solutions were decanted to volumetric glass flasks and filtered through blue band filters (pore size of 2 μm) to polyethylene jars. The filtrates were measured with a flame atomic absorption spectrometer (AAS Varian AA 280 Series, Varian BV, Germany) to determine the concentration of the exchangeable cations Ca^{+2} , K^{+2} , Mg^{+2} , Na^{+2} . The base saturation (BS) was calculated using equation 4.

$$\% BS = \frac{100 * \sum(Na + K + Ca + Mg)(\text{mmol}_c \text{ kg}^{-1})}{CEC (\text{mmol}_c \text{ kg}^{-1})} \quad (\text{Eq. 4})$$

4.2.9 Oxalate-soluble and dithionite-soluble iron and manganese compounds content

The pedogenic iron and manganese compounds were extracted and fractioned by dithionite- and oxalate solutions according to [Mehra and Jackson \(1960\)](#), and [DIN 19684-6](#). To extract oxalate-soluble iron and manganese, 2 g air-dried fine material were mixed with 100 mL of oxalate solution (17.60 g $(\text{COOH})_2$ + 28.40 g $(\text{COONH}_4)_2$ + 1000 mL bidistilled H_2O), and shaken in the dark for 1 h. The obtained suspensions were filtered and decanted into Erlenmeyer flasks. The extraction of dithionite-soluble iron and manganese with replicates was carried out using 2 g fine-grained material after combustion for 4 h at 550 $^\circ\text{C}$ and 50 mL of complex solution A (70.58 g $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$ + 16.80 g $\text{NaHCO}_3 \text{ L}^{-1}$ + 1000 mL bidistilled H_2O). After heating in a water bath to 85 $^\circ\text{C}$, 1 g $\text{Na}_2\text{S}_2\text{O}_4$ was added to the suspensions and stirred for 15 min. The obtained extractions were centrifuged (3000 rpm for 10 min) and decanted in 250 mL volumetric flasks. The residue of the extractions were washed with 20 mL of complex solution B (12.325 g $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O} \text{ L}^{-1}$ + 1000 mL bidistilled H_2O) centrifuged, and supernatant liquids were added to the flask. Afterwards, the volumetric flasks were made up to 250 mL volume with distilled water,

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and the extracts were filtered. Calibrating solutions of Fe and Mn with concentrations from 1 to 5 ppm were used for quality control. The resulting extracts of oxalate- and dithionite-soluble iron and manganese were measured with the flame atomic absorption spectrometer (Varian AA 280 Series, Varian BV, Germany).

4.2.10 Trace metal content

The extraction of Fe, Mn, Zn, Cd, Ni, Cu, As, Pb, Co and Hg was performed using a microwave method (Mars Xpress, CEM GmbH, Germany; [DIN ISO 11466](#)). Sample lots of fine grained and dried soils (1.5 g of mineral material, 0.5 g of organic-rich material) were put into Teflon vessels and treated with aqua regia solution (13.4 mL of HCl 30%, and 3.5 mL of HNO₃ 60%). The extraction of elements Fe, Mn, Zn, Cu, Ni, and Pb from the plants was done by treating 0.25 g of the material, prior oven-dried at temperature 40 °C, with 8 mL of HNO₃ 60%. Extracted solutions were decanted to glass flasks of volume 50 mL for soil samples, and 25 mL for plant material, and made up to the volume by bidistilled water. The obtained extracts were flown through the blue ribbon ashless filters (Whatman, 125 mm, Cat No. 10 300 211) and stored in 50 mL plastic jars for analysis.

The extraction of plant available element fractions of Cd and Pb was carried out according to [DIN ISO 19730:2009-07](#). Air dried, homogenized soil sample was taken in an amount of 10 g, placed into a shaking sample bottle and treated with 25 mL NH₄NO₃ (1 M, of temperature 20 ± 2 °C). The suspension was shaken for 2 h and after, centrifuged (3000 rpm). After 10 min centrifugation, the obtained solution was immediately flown through a membrane cellulose acetate filter (45 µm, VE 100) under vacuum, and collected in polyethylene carboys. Afterwards, the filtered solution was preserved by adding of HNO₃ (1 % from the extracted solution volume).

The element content of Cd, Ni, Cu, As, and Pb was analysed using the AAS Varian AA 280 Series (Germany) with a graphite tube. The elemental content of Fe, Mn, and Zn was detected by flame AAS Varian AA 280 Series (Germany). The content of Hg was detected by a Flow Injection Mercury System (FIMS) (Perkin Elmer AS 90, Shelton, USA; [DIN ISO 16772:2005-06](#)). Results are expressed in mg kg⁻¹ of dry weight (dw).

4.2.10.1 *Quality control*

Data quality was examined on a batch-by-batch basis for each element using standards, laboratory replicates and reagent blanks. The quantification limits of each element (in mg kg⁻¹) are given in Table 4. Two blanks were run in each series of samples.

Table 4: Quantification limits (QL) of the measured trace metals (in mg kg⁻¹).

<i>Element</i>	<i>As</i>	<i>Cd</i>	<i>Co</i>	<i>Cu</i>	<i>Fe</i>	<i>Hg</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
<i>QL</i>	0.13	0.008	0.05	0.04	8.3	0.016	3.33	0.10	0.27	1.33

4.2.11 Data analysis

4.2.11.1 *EDA approach for analysis of the compositional data and data performance.*

Boxplot and scatterplot graphing was performed with SPSS package version 20.0 based on methods of the exploratory data analysis (Tukey, 1977). The exploratory data analysis (EDA) methods are often used when dealing with environmental data (Aitchison, 1982; Aitchison, 2003) and well performed in studies of Reimann et al (2008). Prior to plotting, the element concentrations were log-transformed since the data were strongly right-skewed for the majority of the elements. Spearman's rank correlation analysis was used to determine a relation between detected elements. Non-parametric Mann-Whitney U test was used to reveal the differences of element contents in surface soils, plant species, and between species, respectively. The graphs were produced using the Origin Lab package version 8.6. The maps were produced with the ArcGIS package version 9.3.

4.2.11.2 *Calculation of trace element volumetric concentrations.*

The volumetric trace metal concentrations TM_{vol} (g m⁻³) were calculated in 1 cm-thick slices of the top and bottom horizons of the studied units using equation 5.

$$TM_{vol} = C \times BD \quad (\text{Eq. 5})$$

Where C is trace metal concentration in soil genetic horizon (mg kg⁻¹), and BD is the bulk density of the soil which was calculated as a ratio of the dry mass of an unsaturated soil sample and the volume of the soil sample cup.

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4.2.11.3 Calculation of a coefficient of buffer capacity of top soils

In case of aerial pollution, a considerable part of contaminants precipitates to the top soil horizon, which is usually organic rich. Trace elements differ from each other in their ability to bind to organic matter. Higher buffer soil capacity shows the decrease of the element migration ability. Vodyanitsky et al (2012) suggested to estimate the buffer capacity of an organic rich horizon Bf (%) as the ratio of concentration of a bound element to its content in a soil profile (equation 6).

$$\% Bf = 100 \cdot \frac{(C_A \cdot h_A)}{\sum C_i \cdot h_i} \quad (\text{Eq. 6})$$

Where C_A and C_i are element contents (in mg kg^{-1}) in the top organic rich (A) and i- horizons, h_A and h_i are the horizon depths. The following gradations of buffer capacity are suggested to use: (0-10 %) – *very low*, (10-20 %) – *low*, (20-30 %) – *middle*, (30-40 %) – *high*, and (> 40 %) – *very high*.

4.2.11.4 Calculation of a bioaccumulation coefficient

The bioaccumulation coefficient (BC) is defined as the ratio of trace element content in plant material (C_p) (in mg kg^{-1}) to the trace element concentration in soils in 0-10 cm depth (C_s) (in mg kg^{-1} dw) (Adriano, 2001).

$$BC = \frac{C_p}{C_s} \quad (\text{Eq. 7})$$

Coefficient of bioaccumulation $BC > 1$ suggests that the element accumulation by plant species occurs. If $BC < 1$, the element content in plant species is in deficit.

4.3 Experimental setup to study trace metal distribution in soil columns affected by unidirectional freezing

4.3.1 Soil material for the experiment

For the experiment, soil material at Harburger Berge from a forest site near Harburg (Hamburg) (53° 21' 59 " N, 10° 01' 58" E) without evident influence of trace metal pollution was selected. The sandy material was collected in July of 2012 and stored in plastic bags at 5 °C. Prior to the analyses, a part of the soil material was air-dried and sieved through a 2 mm sieve. The results of laboratory analyses, using methods described in the Subsection 4.2, are shown in Table 5. The preparatory work was initiated by determining the water content in the field-moist sandy material. The grain-size analysis showed that the sandy fraction was dominant in the experimental material. The material was characterized by low organic carbon content, which was favourable for the experiment, because the adsorption capacity of metal ions by organic compounds in the soil material was low. The concentrations of Cd and Pb were low and lay in the same range as the element contents found in sandy soils of the middle floodplain in the Lena River Delta, northern Siberia.

Table 5: Physical and chemical properties of the soil material used in the lab experiment and alluvial soils of the middle floodplain in the Lena River Delta, northern Siberia (Samoylov Island 72° 22' N, 126° 31' E).

Soil characteristics	Experimental soil (Harburger Berge)	Soil of the floodplain (Samoylov Island)
Water content [%]	12.8	—
Texture Index (<i>AG Boden, 2005</i>)	Ss	Ss
Sand (63 < μm < 630) [%]	89.0	91.4
Silt (2 < μm < 63) [%]	8.2	5.8
Clay (μm < 2) [%]	4.6	2.8
pH	5.0	7.2
C [%]	0.3	0.5
Pb [mg kg ⁻¹ dw]	8.0	7.0
Cd [mg kg ⁻¹ dw]	0.07	0.05
Fe [mg kg ⁻¹ dw]	11426	18624
Mn [mg kg ⁻¹ dw]	281	229
Zn [mg kg ⁻¹ dw]	25.1	49.1

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4.3.2 Soil contamination procedure and column preparation

The experiment was based on the contact method of interaction between contaminated and uncontaminated soil material. The experimental column consisted of two polymethylmethacrylate (PMMA) cylinders (PERIGLAS XT, EVONIK Industries) with inner diameters of 5 cm and heights of 3 and 5 cm which were joined during the experiment by means of a cylinder of a bigger diameter. The lower part of the column (5 cm height) was filled with uncontaminated soil material mixed with bidistilled water. The gravimetric water content of the wetted soil was adjusted to an average value of 12.3 %. The upper part of the soil column (3 cm height) was filled with contaminated soil material and afterwards, compacted (Fig. 16a).

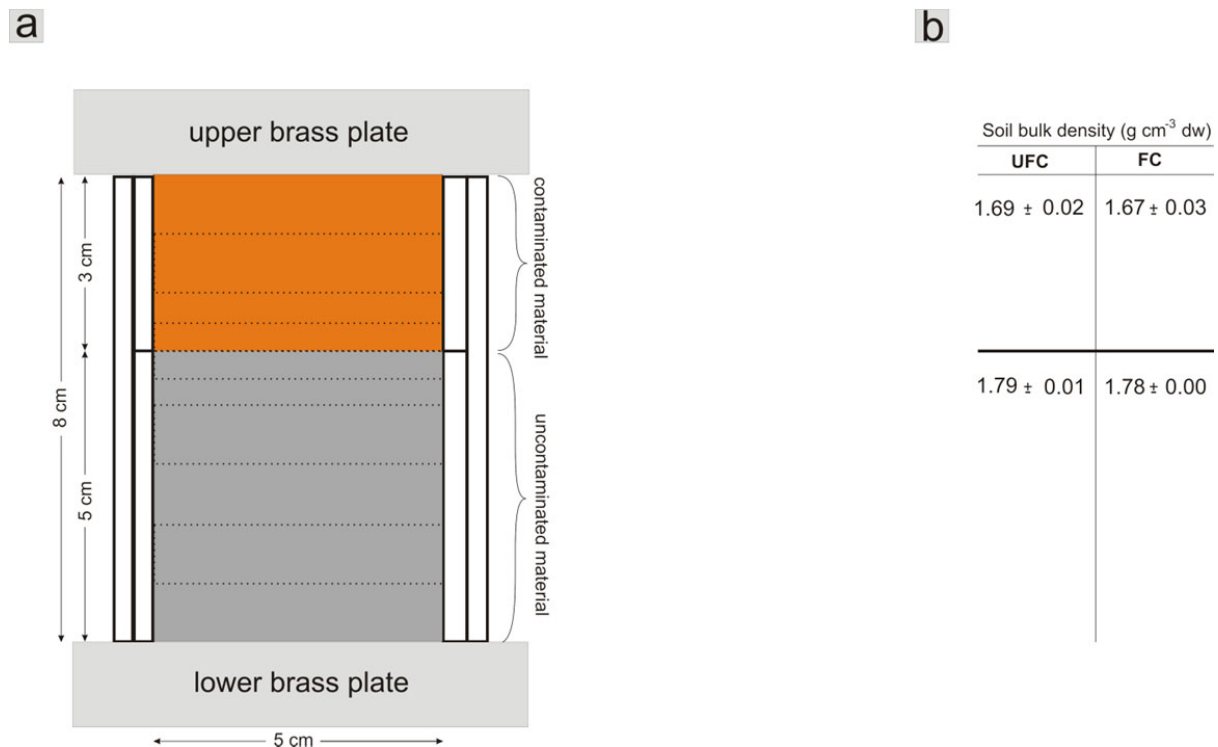


Figure 16: Conceptual scheme of the experimental columns showing: (a) – their design and mode of the column layer slicing shown by horizontal dashed lines and (b) – initial soil bulk density calculated for each soil cylinder of soil columns without freezing (UFC) and soil columns affected by unidirectional freezing (FC) after column construction.

For contamination of the soil material with metals, two standard solutions of lead nitrate ($\text{Pb}(\text{NO}_3)_2$ in H_2O : 1000 mg of Pb per ampoule; standard ID 10 9969, Titrisol) and cadmium

chloride (CdCl_2 in H_2O : 1000 mg of Cd per ampoule; standard ID 10 9960, Titrisol) were chosen. The experimental soil material was mixed with Pb and Cd solutions. After mixing, the average concentrations in the soil material reached $52.9 \pm 0.8 \text{ mg kg}^{-1}$ of Cd and $534 \pm 7.9 \text{ mg kg}^{-1}$ of Pb, respectively ($n = 8$). It is necessary to note, that such high concentrations of Cd and Pb, as used in the experiment, are unlikely to be found in natural environments. High concentrations of Pb and Cd were taken to ensure that the metal concentrations within whole soil column depth after the experiment would be detectable using flame AAS.

The equilibrium pH of the soil after contamination was 3.7. The average gravimetric water content of contaminated soil material was 13.2 %. After packing the columns, the tops and bottoms were sealed by laboratory film (Parafilm M, $4'' \times 125''$, Bemis) to prevent water loss. For the column test, 12 soil columns were constructed. Two of them were used only for temperature measurements. After the column preparation, soil bulk density was calculated for all experimental columns and ranged from 1.63 to 1.71 g cm^{-3} (soil dw) for the upper soil cylinders and from 1.78 to 1.80 g cm^{-3} (soil dw) for the lower soil cylinders (Fig. 16b).

4.3.3 Column experiments

The experimental setup consisted of two insulated wooden boxes (Fig. 17). Each box contained six identical soil columns which were fixed between two brass plates, thus providing good contact between the plates and the upper and lower face of the soil columns (Fig. 16a). One of the six columns in each box was equipped with three temperature sensors at 2, 4, and 6 cm depth. These instrumented columns were not used in later analyses. Therefore, each experiment comprised five replicates. The soil columns of the control BOX 1 were set between two brass plates at room temperature over the experiment time. The lower brass plate of the BOX 2 was cooled by means of a closed cycle cooling system (JULABO F-32-HE, Seelbach, Germany). The coolant flow rate was controlled manually, and the coolant temperature was controlled by a programmable thermostat of the cooling system. The temperature was gradually decreased, starting at room temperature and decreasing to $+4 \text{ }^\circ\text{C}$ in step one at the interval of 3 h, to $-3 \text{ }^\circ\text{C}$ in step two of the interval of 1 h, and finally, to $-5 \text{ }^\circ\text{C}$ in step three of the interval of 12 h and lasted until the end of the experiment (Fig. 18). At the same time, the soil columns of BOX 1 were kept at room temperature. The soil temperature was recorded each 10 min and saved on a DL2 data logger (DELTA-T DEVICES Ltd, Cambridge, UK). The duration of the experiment was 443 h.

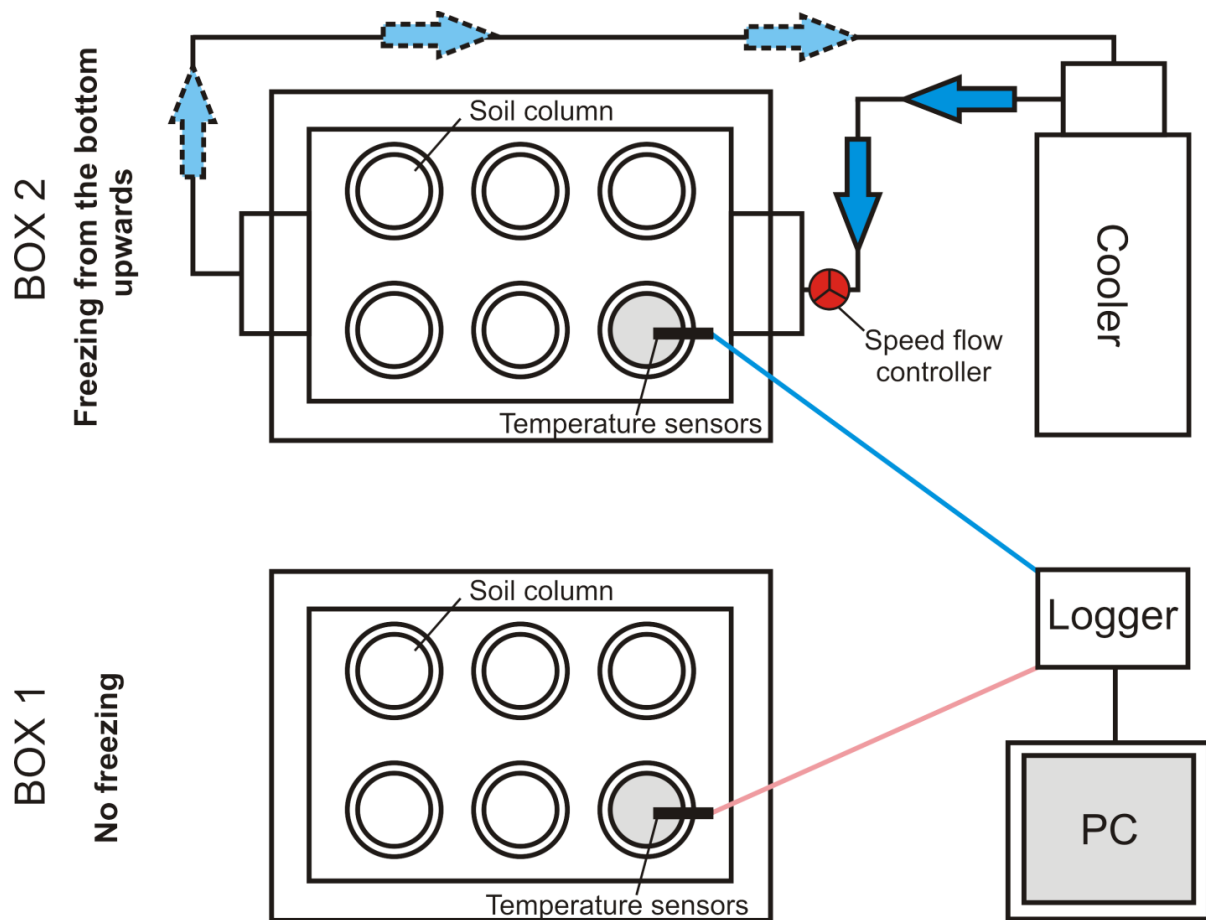


Figure 17: A scheme showing the experimental setup of two simultaneous column experiments. The experiment consisted of two thermally insulated wooden boxes each comprising six identical soil columns. One column of each box was instrumented for temperature measurements and was not used for laboratory analyses. During the experiment, soil columns of BOX 1 were kept at room temperature and the columns of BOX 2 underwent the unidirectional freezing from the bottom upwards.

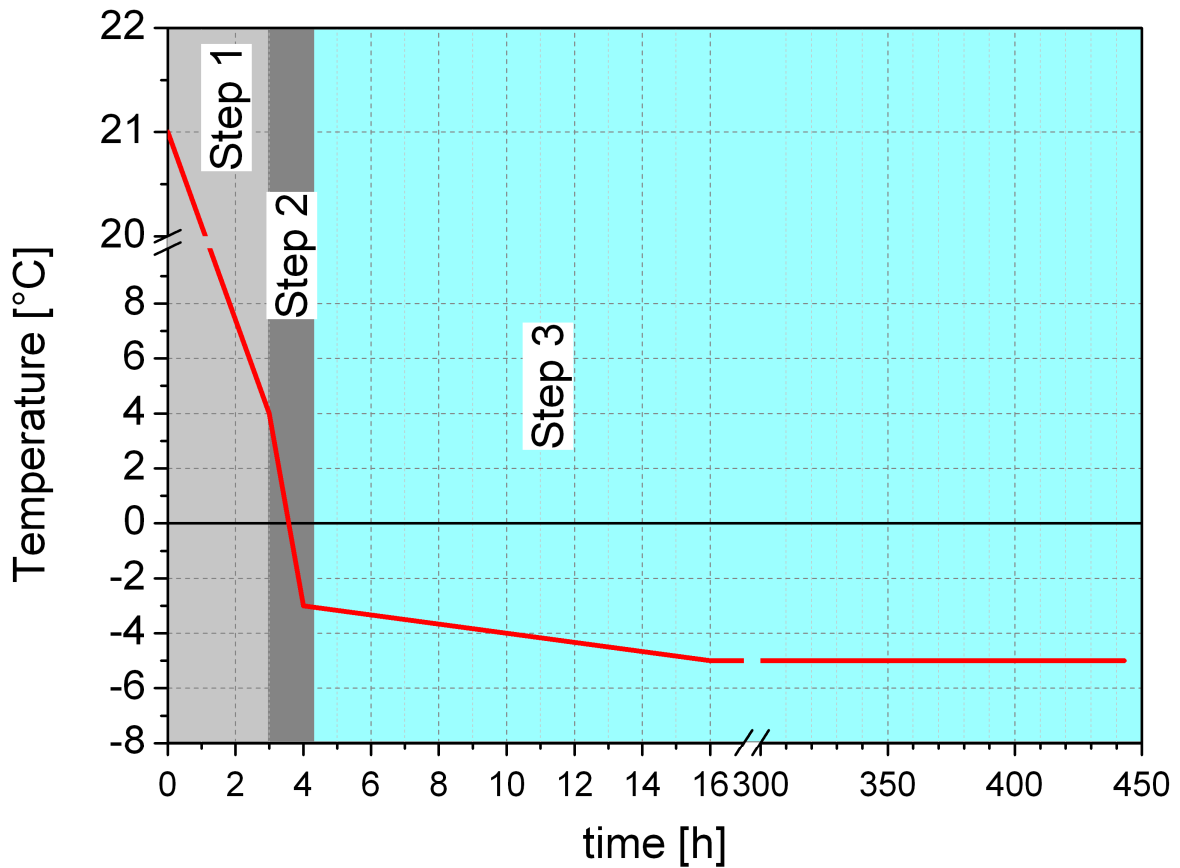


Figure 18: Stepwise decrease of the coolant temperature controlled by a programmable thermostat of the cooling system JULABO.

4.3.4 Soil sampling after the experiment

After the experiment, the soil columns from BOX 2 were sampled in a cooling room at the temperature of +5 °C, and the columns from BOX 1 were sampled at room temperature. The upper and lower parts of soil columns were separated and of the soil columns were removed from the PMMT cylinders. The soil columns were cut into slices of 0.5 cm and 1.0 cm width, respectively (Fig. 16a). The sampled soil layers were analysed for water content and trace metal concentrations by the methods described in Subsections 4.2.3 and 4.2.10, respectively.

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4.3.5 Mass balance calculation

The mass balance calculation was carried out to estimate the accuracy of the laboratory analyses. It has been performed by calculating the deviation D (in %) of the sum of the initial metal content (m_i^0) and the sum of the element content (m_i^f) after the experiment within the whole soil column (in mg), where i is a number of soil layer in a column equal to 10 (equation 8).

$$\% D = 100 \cdot \frac{(\sum_{i=1}^{10} m_i^0 - \sum_{i=1}^{10} m_i^f)}{\sum_{i=1}^{10} m_i^0} \quad (\text{Eq. 8})$$

According to the mass balance calculation results, the average percentage of loss of elements in experimental columns without freezing (UFC) amounted to 3.2 % for Cd and 2.7 % for Pb which could be explained by the loss of soil material during sectioning, while for soil columns affected by unidirectional freezing, the deviation varied from 4.5 % for Cd to 1.3 % for Pb, respectively.

4.3.6 Calculation of relative element concentration decrease in soil columns

A relative decrease of element concentrations in soil columns (ε) is determined as the percentage ratio of the difference between the initial (C_i^0) and final (C_i^f) element concentrations and the initial element concentration (C_i^0) at i -soil layer (equation 9).

$$\% \varepsilon = 100 \cdot \frac{C_i^0 - C_i^f}{C_i^0} \quad (\text{Eq. 9})$$

4.3.7 Calculation of available trace metal fraction

In order to shed light on metal migration ability in soils without and under the influence of freezing, available fractions of Cd and Pb were calculated for each column layer. The concentrations were calculated as a ratio of the element concentrations (r_c) resulting from two extraction procedures: (1) digestion by aqua regia (C_{AR}) and (2) by ammonium nitrate (C_{AN}) (Eq. 10). The digestion method by aqua regia solute represents the extraction of nearly total element

content from the soil matrix, while the digestion method by ammonium nitrate provides the information about the content of potentially plant available element forms in soils.

$$r_C = \frac{C_{AN}}{C_{AR}} \quad (\text{Eq. 10})$$

5. Results and discussion

5.1 Characterization of permafrost-affected soils of the investigated area

5.1.1 Soils of the Lena River Delta Region and its hinterland

According to the Soil Taxonomy Classification (Soil Survey Staff, 2010), all studied soils were described as Gelisols (Tab. 6). They belong to the following great groups: (1) Turbel suborder which comprises *Histoturbels*, *Aquiturbels*, and *Psammenturbels*, (2) Orthel suborder which consists of three great soil groups: *Aquorthels*, *Historthels*, and *Haplorthels*, and (3) Histel suborder which includes only one great soil group called *Fibristels*. According to the Russian classification of Elovskaya (1987), all soils of the units between 73° and 70° N (H-2) belong to the Permafrost type (Tab. 6) (Elovskaya, 1987; Desyatkin & Teterina, 1991; Pfeiffer et al, 2000; Desyatkin et al, 2009; Ivanova et al, 2012). The soil suborder at the southernmost site of the hinterland (H-3) was determined to be a Cryogenic soil (Elovskaya, 1987). The soil properties of this unit differ from other soils of the Lena River Delta and the area of the Chekanovsky Ridge slopes as it was developed underneath a forested area. The investigation sites, being developed on various geomorphological formations, differed from each other in terms of the thawed layer depth. The minimum soil thaw depth of 24 cm (on 18.8.2009) was determined for *Typic Aquorthel / Permafrost Silty-Peat-Gley* developed on the Sardakh Island. The thaw depth of the *Typic Aquorthel / Permafrost Alluvial Turfness Typical* on the floodplain of Samoylov Island reached a maximum of 91 cm on 20.9.2010 (Tab. 6).

Soil properties of the selected soil profiles of the Lena River Delta and its hinterland are shown in Figure 19. The studied soils were characterized by slightly acidic and neutral conditions excluding two units – of the third terrace (3T-1) and floodplain (MF-1) (Appendix, Tab. III). For these sites, the pH was determined to be slightly alkaline. The grain-size composition within all geomorphological units comprised mainly fine-grained sand fractions (Appendix, Tab. III). The majority of studied profiles were characterized by gleying properties within the mineral horizons. The highest median value of the sand fraction was found on the second terrace (site 2T-1) (Fig. 19b). The site 3T-2 of the third terrace showed the lowest fine-grained sand fraction content but significantly high silt fraction content. The southernmost unit H-3 of the latitudinal transect was similar to the 3T-2 study site in terms of texture composition, as both consist primarily of the silt

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fraction. The data of pH and grain-size composition were similar to data reported for soils of the Lena River Delta by [Desyatkin & Teterina \(1991\)](#).

Table 6: Soil classification of investigation sites of the Lena River Delta and its hinterland according to [Soil Survey Staff \(2010\)](#) and Russian soil classification ([Elovskaya, 1987](#)).

Sites ID	Thaw depth, cm	The US Soil Taxonomy (Soil Survey Staff, 2010)	Russian Soil Classification (Elovskaya, 1987)
3T-1	39	Folistic Haplorthel	Permafrost tundra Turfness-Gley Typical
3T-2	24	Typic Aquorthel	Permafrost tundra Silty-Peat-Gley
2T-1	57	Typic Psammenturbel	Permafrost tundra Alluvial Turfy Typical
1T-1	30	Typic Aquiturbel	Permafrost tundra Peatish-Gley Typical
1T-Rim1	61	Typic Aquiturbel	Permafrost tundra Turfness-Gley Typical
1T-Ce1	40	Typic Fibristel	Permafrost Peat
1T-d	36	Typic Historthel	Permafrost tundra Peat-Gley
HF-Rim2	40	Typic Histoturbel	Permafrost tundra Peatish-Gley
HF-Ce2	50	Typic Histothel	Permafrost tundra Peat-Gley
MF-1	91	Typic Aquorthel	Permafrost Alluvial Turfness Typical
H-1	26.5 ± 3.5	Ruptic Historthel	Permafrost tundra Peat
H-2	39	Typic Aquorthel	Permafrost tundra Silty-Peat-Gley
H-3	49	Typic Haplorthel	Cryogenic Soil

The organic carbon content showed a high spatial variability among all investigated units (Appendix, Tab. III) which has been also reported in other studies of the Arctic region (e.g. [Bockheim et al, 2003](#)). Median contents of carbon varied from 1 % on the second terrace to 40 % on the H-1 study site. The C/N ratio was higher for the sites located in the Hinterland which could suggest a higher organic matter accumulation due to a slow process of organic matter decomposition because of the different plant species composition in comparison with the deltaic region (predominance of shrubs) and a presumably higher biomass production during the warm period.

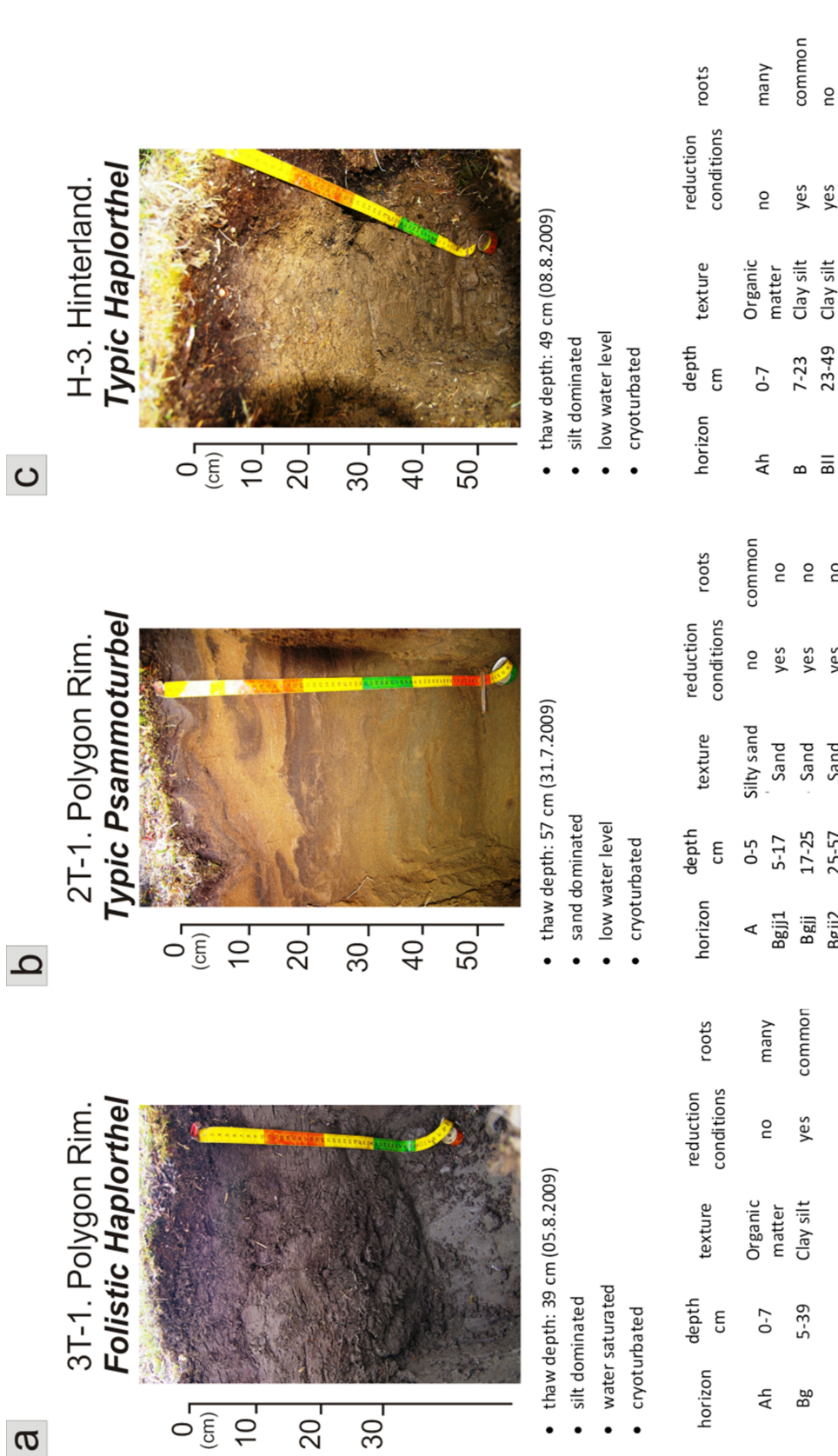


Figure 19: The investigated soils of the Lena River Delta region and its hinterland and their properties: (a) – Third terrace: *Folistic Haplorthel*, (b) – Second terrace: *Typic Psammoturbel*, and (c) – Hinterland: *Typic Haplorthel*. The soil names were given according to the US Soil Taxonomy (Soil Survey Staff, 2010).

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Samoylov Island

The results of standard soil parameters on Samoylov Island showed differences in their distribution on different micro-relief forms. Polygon centres had a more acidic soil reaction than polygon rims. This difference is most evident for advanced stages of polygon development found on the first terrace (Fig. 20a). All values of pH obtained in this study were in agreement with data published for the soils of Samoylov Island previously (Yakshina, 1999b; Kutzbach, 2000; Sanders, 2011).

The highest median values of organic carbon content as well as of the C/N ratio were observed for polygon centres also indicating lower rates of organic matter decomposition there (Fig. 20a and 20b). The lowest contents of organic carbon were observed in alluvial soils developed in the middle floodplain at the depth 8 – 29 cm (soil horizons A₂, Bg₁, and Bg₂) (Fig. 20c). The values of OC in these horizons varied from 0.3 to 0.8 %. The dominant fraction of mineral horizons of the studied profiles was fine-grained sand. The polygon rim 1T-Rim1 was of exceptional interest because the processes of cryoturbation were clearly pronounced. Here, median contents of clay and silt material within the soil profile were higher in comparison to the other study sites.

The soil profile of the study site 1T-d of Samoylov Island located nearby the Fish Lake (Fig. 12) was determined as *Typic Historthel*. Physical and chemical analysis of soil core (taken in summer of 2009) of this studied site showed, that it differed from the other sites by notably high OC contents in the surface layers. The OC content in average amounted to 22 % at the first 6 cm depth of the investigated soil profile. With increasing depth, the values for OC gradually decreased and reached the minimum values of 2 % in B_{hsg} horizon at the depth of 17-20 cm. The soil pH acidity of the surface horizon was distinctly less than the underlying soil layers dropping from values of 5.3 in O_i horizon to 6.9 in O_e horizon (Fig. 20d). The highest of C/N ratio were also found in the surface horizon and reached the maximum value at 3-6 cm depth.

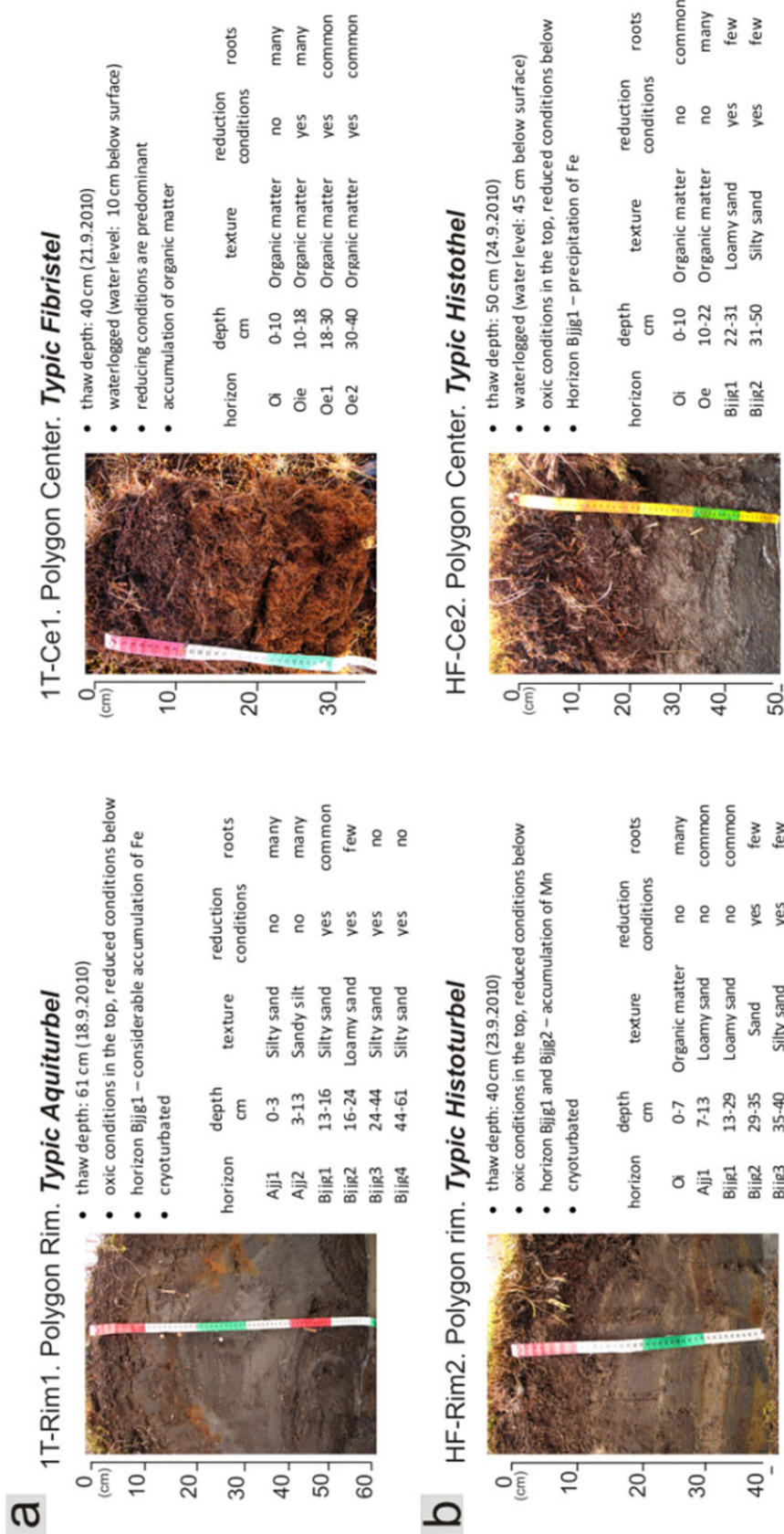


Figure 20: The investigated soils of Samoylov Island and their properties: (a) – *Typic Aquiturbel* (polygon rim) and *Typic Fibristel* (polygon centre) of the first terrace, (b) – *Typic Histoturbel* (polygon rim) and *Typic Histothel* (polygon centre) of the high floodplain, (c) – *Typic Aquiturbel* of the middle floodplain, and (d) – *Typic Histoturbel* – the investigated soil profile of 1T-d located on the first terrace (former location of the EDDY covariance station). The soil names are given according to the US Soil Taxonomy (Soil Survey Staff, 2010).

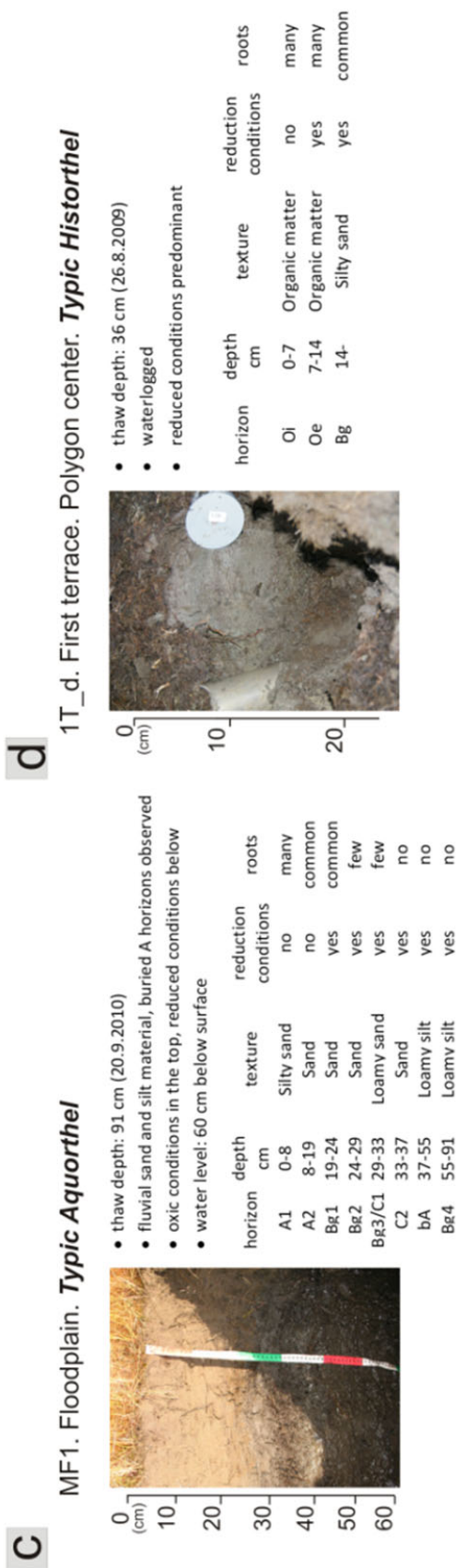


Figure 20: Continued

A detailed study of the soil profiles located on the first terrace (site 1T-Rim1) and middle floodplain (site MF-1) were carried out. The electrical conductivity (EC), cation-exchange capacity (CEC), abundance of basic cations (in $\text{cmol}_c \text{ kg}^{-1}$), were determined in cm-wise soil layers of these profiles. High electrical conductivity (EC) was observed in the surface soil layers of both *Typic Aquiturbel* and *Typic Aquorthel* (Fig. 21). In both soil profiles, EC gradually decreased with the depth being higher in 1T-Rim1. The minimum values of EC were observed in sand-dominant layers of the soil profile MF-1. The minimum values of EC for the soil profile of the first terrace were found in layers composed from silty-sand fraction and starting from the depth of 20 cm the values of EC again increased progressively for both profiles but especially for *Typic Aquorthel*. Thus, the values of EC clearly reflect the soil texture of investigated soil profiles.

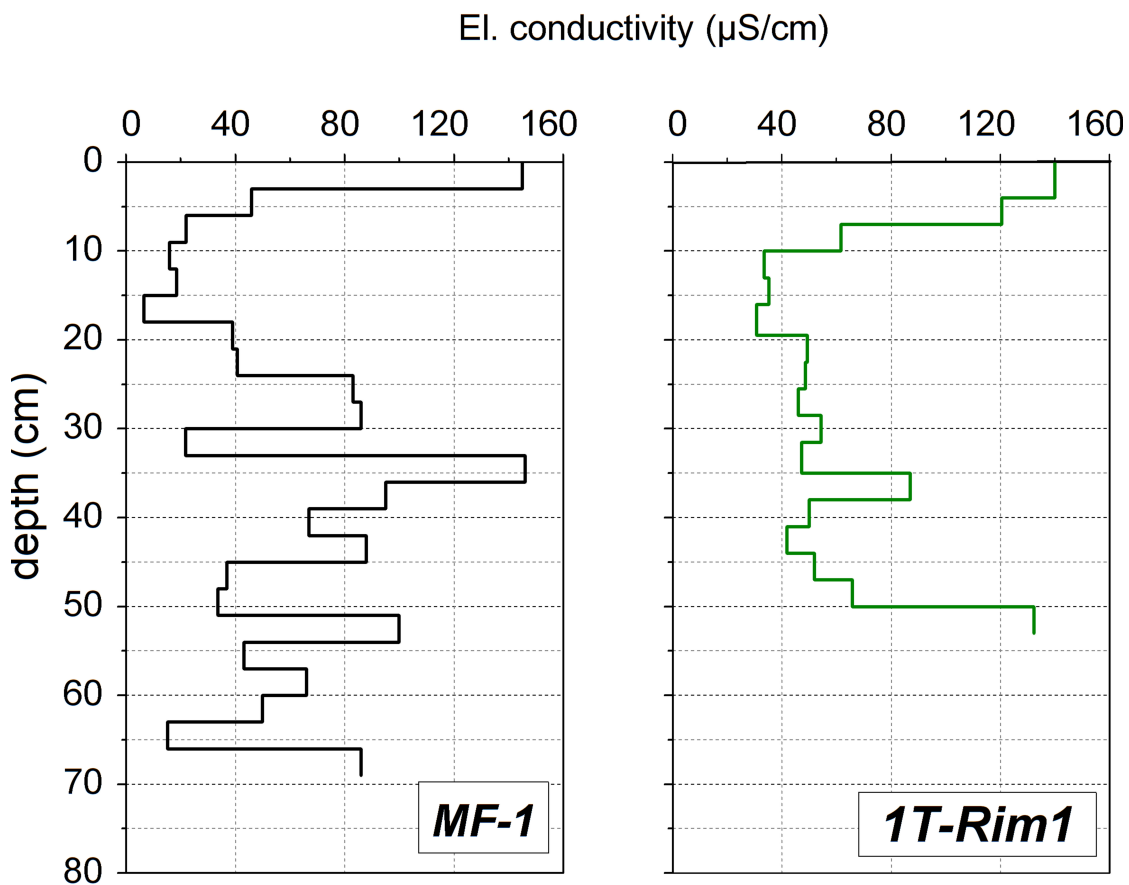


Figure 21: Vertical distribution of the electrical conductivity in soil profiles of *Typic Aquorthel* (MF-1 of the middle floodplain) and *Typic Aquiturbel* (polygon rim 1T-Rim1 of the first terrace) on Samoylov Island.

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The abundance of water soluble ions for both soil profiles composed the following range: $\text{Ca}^{2+} > \text{Mg}^{+2} > \text{K}^{+} > \text{Na}^{+}$ (Fig. 22). *Typic Aquorthel* of the middle floodplain was characterized by higher concentrations of all base ions in comparison with *Typic Aquiturbel* developed on the first terrace. Significant differences were found only for sodium content (non-parametric Mann-Whitney U test, $p < 0.05$). The median value of CEC for the site of the middle floodplain was slightly less than for the site of the first terrace (the values for these sites amounted to 10.9 and 11.1 $\text{cmol}_c \text{ kg}^{-1}$, respectively). Variations of vertical distribution of CEC and the base cation abundance were observed for both studied soil types. Minimum values of all base cations in soil profile of the middle floodplain were observed at the depth of 6 – 24 cm. The soil layers at that depth were formed by fine-to-middle sand fraction which usually has no capacity to exchange cations because of a low ability of sand particles to have an electrical charge. With increasing depth, the abundance of all base cations also increased, reaching the maximum values at the depth of 43-45 cm. The flushing regime and the texture of *Typic Aquorthels* probably play a key role in leaching of bases from the surface layers downwards to the bottom horizons where they can precipitate. The soil of MF-1 was characterized by high values of base saturation (BS) (100 %) and pH (> 7.0), which can indicate the predominance of carbonates in these soils. As it was noted by [Ping et al \(2005\)](#), high values of pH and BS characterize soils which are carbonate saturated and calcium carbonate buffered. It may be possible, that annual inundation events serve as an additional source of carbonates for these soils. According to [Chetverova et al \(2013\)](#) the waters of the Lena River belong to hydrocarbonate-calcium type of water (classification of [Alekin, 1970](#)). The dominant ions of Ca^{+2} in the Lena River water reached mean concentrations of 12.3 mg L^{-1} . Elevated values of CEC in the surface soil layers of *Typic Aquiturbel* (10 – 12 $\text{cmol}_c \text{ kg}^{-1}$) were changed to the minimum values at the depth of 20-30 cm. At that layer which was characterized by a dominance of loamy-to-silty sand fractions, the pH value dropped from 6 to 4.9. However, BS was not changed significantly (from 100 % to 98 %). The maximum values of CEC were observed for the bottom horizons overlying the permafrost table and amounted to 18.0 $\text{cmol}_c \text{ kg}^{-1}$. This finding may suggest that the ions contained in the water solution were excluded from water during the ice lens formation and accumulated above the permafrost table ([Hallet, 1978](#); [Ostroumov et al, 1998](#)).

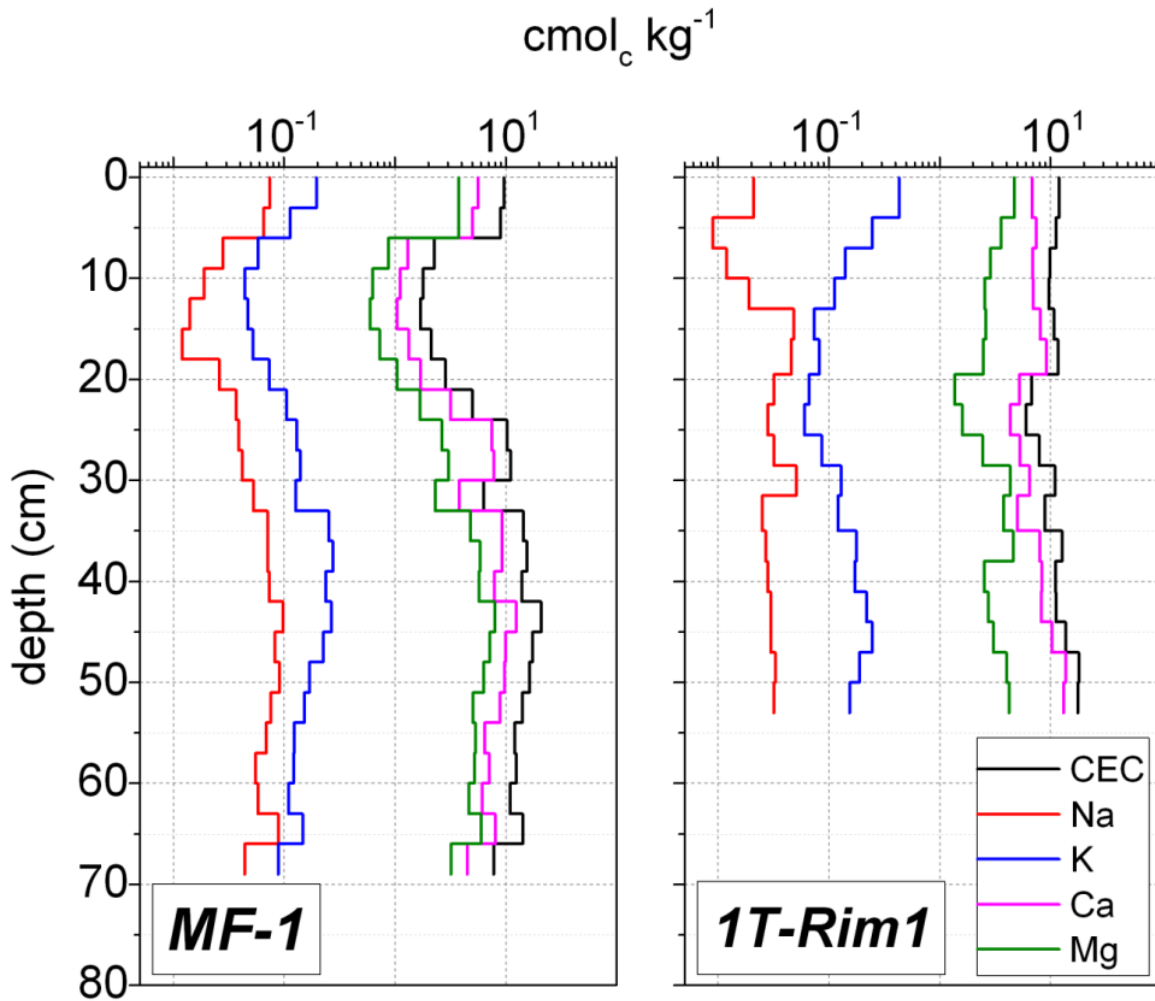


Figure 22: Vertical distribution of water soluble ions and cation exchange capacity (CEC) in two soil profiles *Typic Aquiturbel* (polygon rim 1T-Rim1 of the first terrace) and *Typic Aquorthel* (MF-1 of the middle floodplain) on Samoylov Island.

Figure 23 shows a relationship between CEC and organic matter (OM) content for the soil profiles of the middle floodplain and the first terrace. For both soil profiles a tendency of increase of CEC values with increase of OM content was observed. It is especially evident for the study site MF-1 which was not affected by the processes of cryoturbation. In both soil profiles a significant correlation was found between soil CEC and the content of organic matter (Spearman's rank correlation, $r = 0.91$, $p < 0.01$, for both profiles). Similar relationship between these two soil characteristics were found in [Ping et al \(2005\)](#) for the southern foothills of the Arctic Alaska Range.

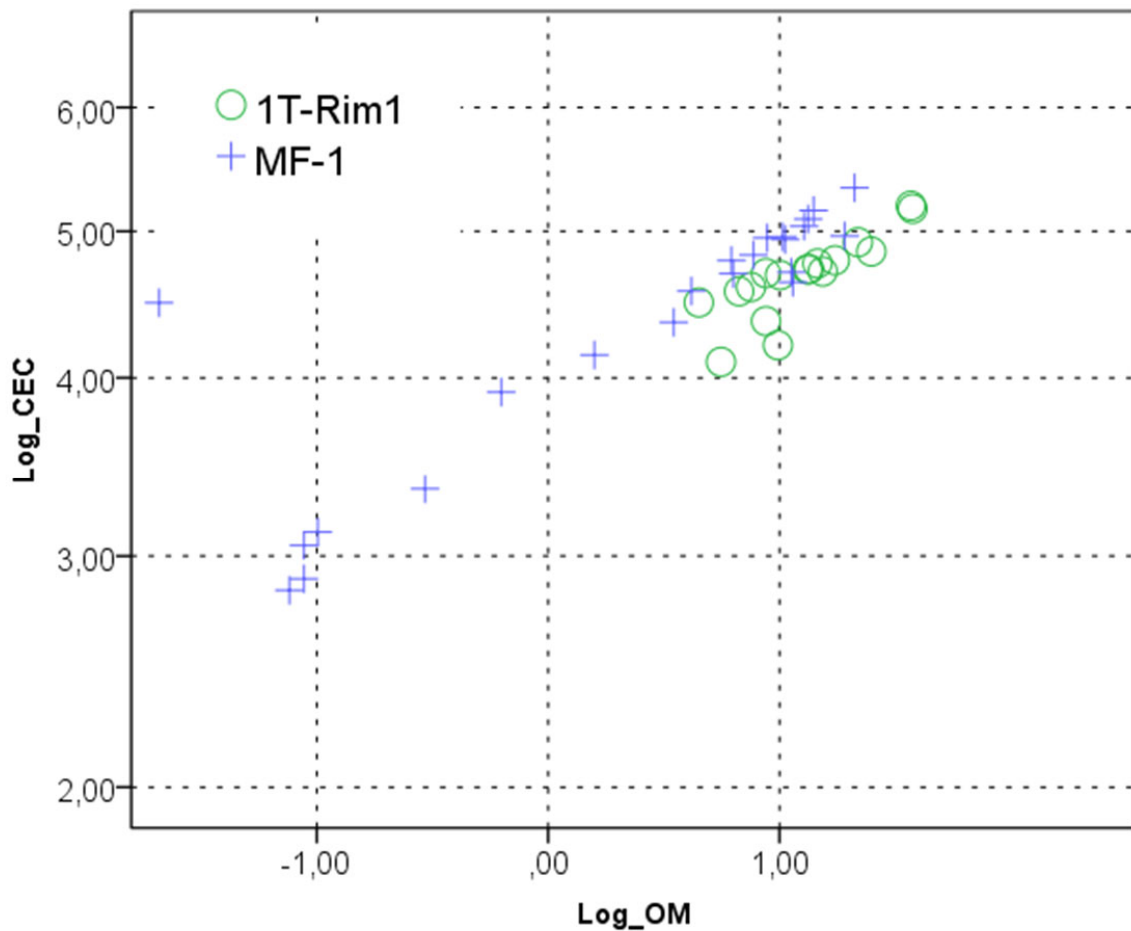


Figure 23: Scatterplot which shows the relationship between CEC and OM content for two soil profiles: *Typic Aquiturbel* (polygon rim 1T-Rim1 of the first terrace) (green circle) and *Typic Aquorthel* (MF-1 of the middle floodplain) on Samoylov Island (blue criss-cross). Spearman's rank correlation, $r = 0.91$, $p < 0.01$.

5.1.2 Soils of the Tiksi area

Figure 24 shows the diversity of the selected soil profiles studied around the Tiksi area. All investigated soil profiles of the Tiksi area were developed on eluvial argillaceous shale. Most soil profile depths were relatively shallow (20 – 30 cm). Only several soil profiles, located to the north from Tiksi settlement, reached the depth of 40 cm and deeper (Tab. 7). The Tiksi area was characterized by a variety of soil types. According to the US Soils Taxonomy (Soil Survey Staff, 2010) most of soils being developed in depressed micro relief forms were described as Orthels and Histels. Soils of slopes and elevated forms of a micro relief belonged mainly to Turbel

suborder. The major organic horizons were defined as: *Oi* and *Oie* depending on the stages of decomposition of organic material. According to the Russian soil classification (Elovskaya, 1987), all investigated soils of the Tiksi area belonged to permafrost type. Cryoturbation processes were clearly defined for soils of slopes and elevated forms of micro-relief. Comparing the US soil classification with Russian soil classification by Elovskaya (1987) no evident consistencies in soil type diagnostics for all soils could be found. However, some similarities for study sites TH4 and TH11 (highlighted in green), and TH5 and TH15 (highlighted in red) were observed (Tab. 7).

The detailed description of all soil profiles is shown in Appendix (Tab. IV). Texture classes derived from the laboratory analysis ranged from sandy loam to silty clay. In many cases, the loam fraction was dominant for the most of soil profiles of this area. Mineral horizons of the study sites TH1 and TH4 were dominated by silty clay fraction. The study site TH6 distinguished from other site by dominance of more light sandy loam fraction in its profile.

The median pH of the studied soil profiles ranged from 4.5 to 6.8. Generally, most of the soils were characterized by reducing conditions having acidic or neutral environmental reaction. The lowest pH median value was found at the TH11 study site. The highest median value of pH was found at the TH12 study site. The investigation sites were arranged into four groups located in northern (TH9, TH10, TH11, and TH14), western (TH3, TH4, and TH5), eastern (TH8, TH12, TH13 and TH15), and southern directions (TH1, TH2, TH6, and TH7) from the Tiksi settlement. Boxplots with pH values for four determined soils groups showed that eastern sites differed significantly from southern, western, and northern sites (Fig. 25). The soil profiles of this site were characterized by slightly acidic and neutral soil conditions, which is likely due to input of sea aerosols. Generally, low median values of EC were found for the southern sites. The surface horizons of all studied sites showed distinctly high electrical conductivity ranging from 86 $\mu\text{S cm}^{-1}$ to 320 $\mu\text{S cm}^{-1}$. With increasing depth, EC values gradually decreased and ranged in B-horizons from 10 $\mu\text{S cm}^{-1}$ to 54 $\mu\text{S cm}^{-1}$. The site TH14 which was located in vicinity to the Bulunkan Gulf was an exception with a higher value of reached 116 $\mu\text{S cm}^{-1}$ for the bottom B-horizon.

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Table 7: Soil classifications of investigated sites of the Tiksi area according to Soil Survey Staff (2010) and Russian soil classification (Elovskaya, 1987).

Sites ID	Thaw depth, cm	Micro-relief form	Soil Survey Staff (2010)	Russian Soil Classification (Elovskaya, 1987)
TH1	23	Depression	Lithic Aquorthel	Permafrost tundra peat-gley soil on eluvial argillaceous shale
TH2	30	Slope	Lithic Haploturbel	Permafrost tundra cryoturbated soil on eluvial argillaceous shale
TH3	25	Upper slope	Ruptic Histoturbel	Permafrost tundra gleyic soil cryoturbated on eluvial argillaceous shale
TH4	22	Slope	Ruptic-Histic Aquiturbel	Permafrost tundra peat-gley cryoturbated soil on eluvial argillaceous shale
TH5	22	Depression	Lithic Historthel	Permafrost tundra silty peatish-gleyic soil on eluvial argillaceous shale
TH6	22	Depression	Typic Historthel	Permafrost tundra turf-gleyic soil on eluvial argillaceous shale
TH7	23	Depression	Ruptic Historthel	Permafrost tundra silty peatish-gleyic soil on eluvial argillaceous shale
TH8	26	Slope	Ruptic-Histic Aquiturbel	Permafrost tundra peatish-gley cryoturbated soil on eluvial argillaceous shale
TH9	12	Depression	Lithic Umbrorthel	Permafrost tundra turf soil on eluvial (sedentary) argillaceous shale
TH10	37	Elevation	Lithic Histoturbel	Permafrost tundra turf-gleyic cryoturbated soil on eluvial argillaceous shale
TH11	46	Elevation	Ruptic-Histic Aquiturbel	Permafrost tundra silty-gley cryoturbated soil on eluvial argillaceous shale
TH12	28	Slope	Ruptic-Histic Aquorthel	Permafrost tundra cryoturbated peat-gley soil on eluvial argillaceous shale
TH13	38	Slope	Lithic Aquiturbel	Permafrost tundra turf-gley cryoturbated soil on eluvial argillaceous shale
TH14	44	Elevation	Lithic Aquorthel	Permafrost tundra turf-gley cryoturbated soil on eluvial argillaceous shale
TH15	16	Depression	Lithic Historthel	Permafrost tundra silty peatish –gleyic soil on eluvial argillaceous shale

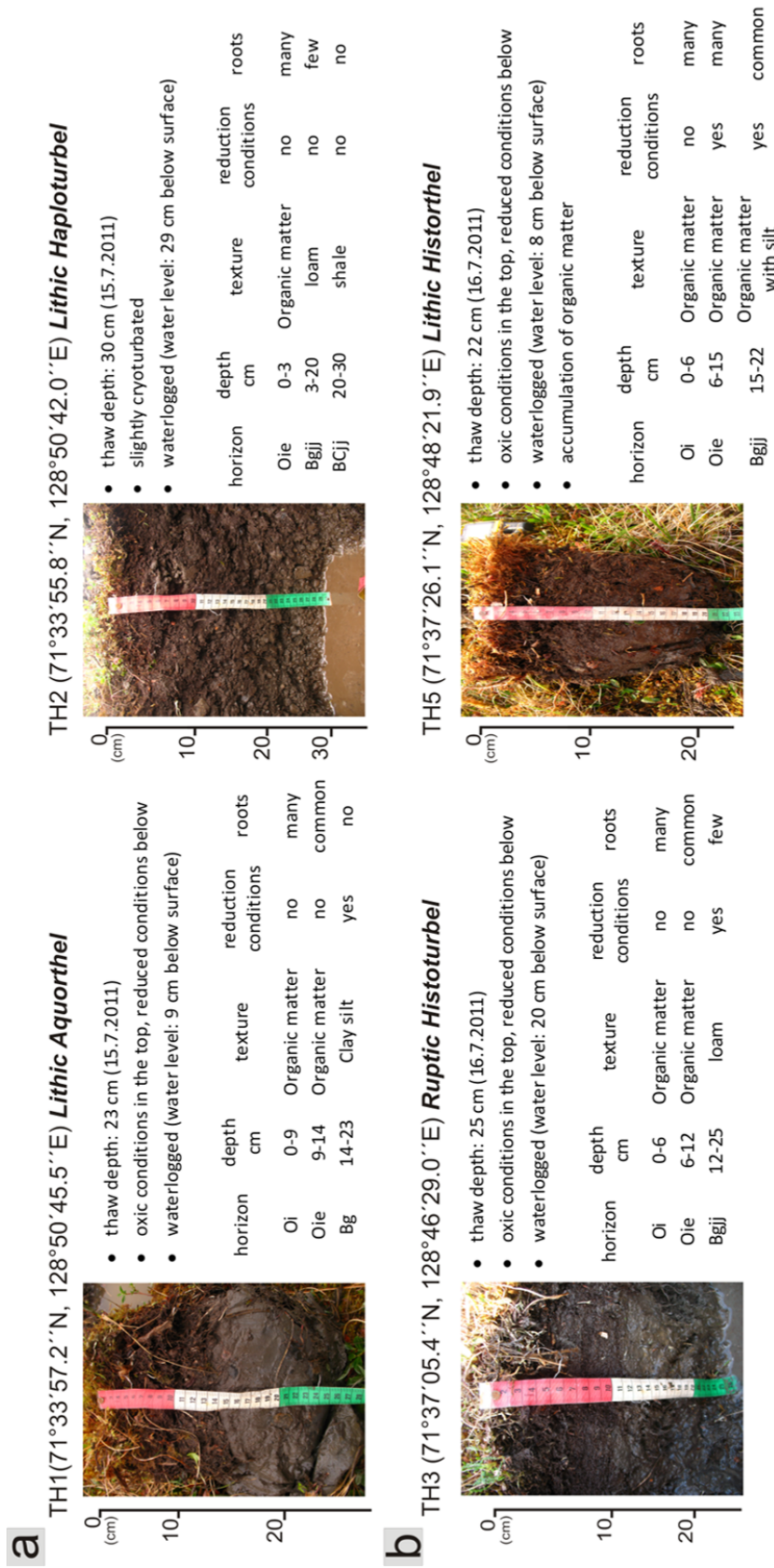


Figure 24: Selected soil profiles of the Tiksi area and their properties: (a) – *Lithic Aquorthel* and *Lithic Haploturbel* of the southern site, (b) – *Ruptic Histoturbel* and *Lithic Historthel* of the western site, (c) – *Ruptic-Histic Aquiturbel* and *Lithic Aquorthel* of the northern site, and (d) – *Ruptic-Histic Aquorthel* and *Lithic Aquiturbel* of the eastern site. The soil type names are given according to the US Soil Taxonomy (Soil Survey Staff, 2010).

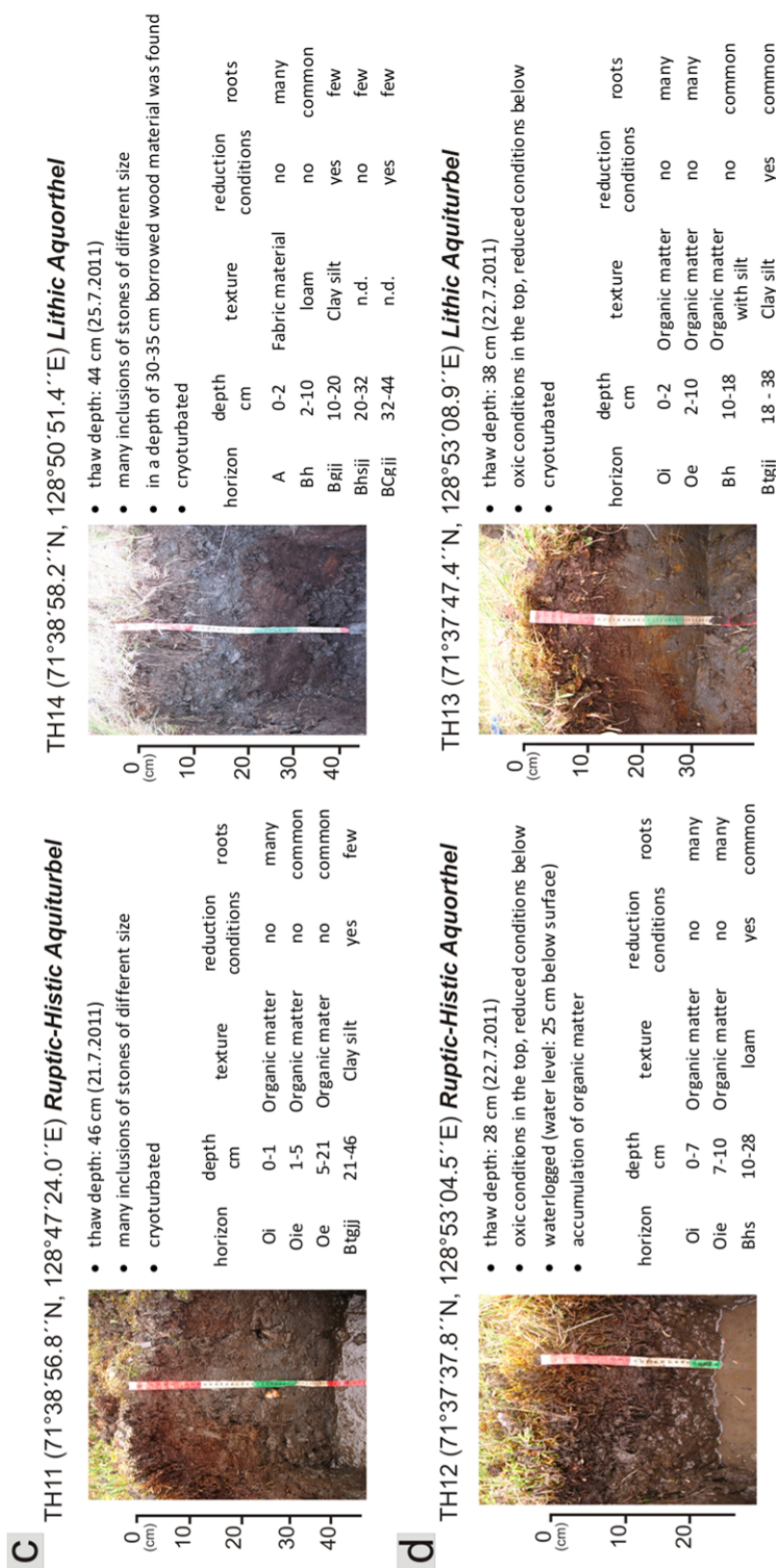


Figure 24: Continued.

No particular difference in carbon and nitrogen content between the sites was found. The surface soil horizons were generally enriched by organic matter. Minimum carbon content in surface soils was found for study sites TH2, TH6, TH9, and TH14, and amounted to 8 – 12 %. Surface soils of southern sites (remote from Tiksi settlement) were characterized by the lowest carbon content, whereas the surface horizons of eastern and western sites had particularly high in carbon. The median value of total organic carbon for these sites was 28 %. At the northern sites, B-horizons were characterized by higher median values of carbon content (Fig. 26). Similar results were found for the nitrogen content in the surface and B-horizons. The highest median values of nitrogen were found in surface soils for groups of eastern and western sites amounted to 1.2 % and 1.5 %, respectively. The highest median value of nitrogen in B-horizon was observed for soils of the northern sites group. Generally, the C/N ratio for all groups of investigation sites was higher in surface horizons than in B-horizons suggesting a higher abundance of organic matter and lower rates of its decomposition in the top soils. The highest variability of C/N ratio was found at the northern sites, which reflects the cryoturbation process development.

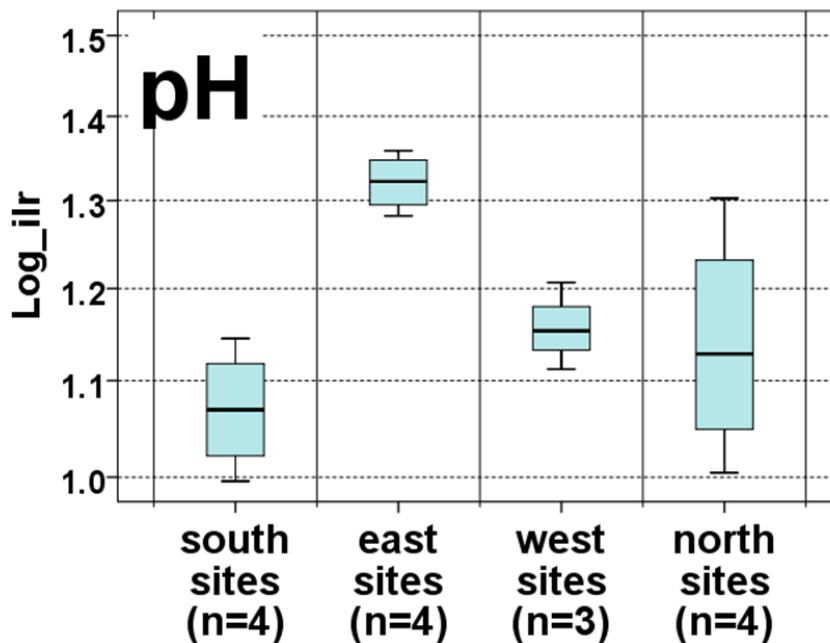


Figure 25: Boxplot comparison of pH values in surface soils of four study groups located around the town Tiksi. Note that pH values were log-transformed prior to plot.

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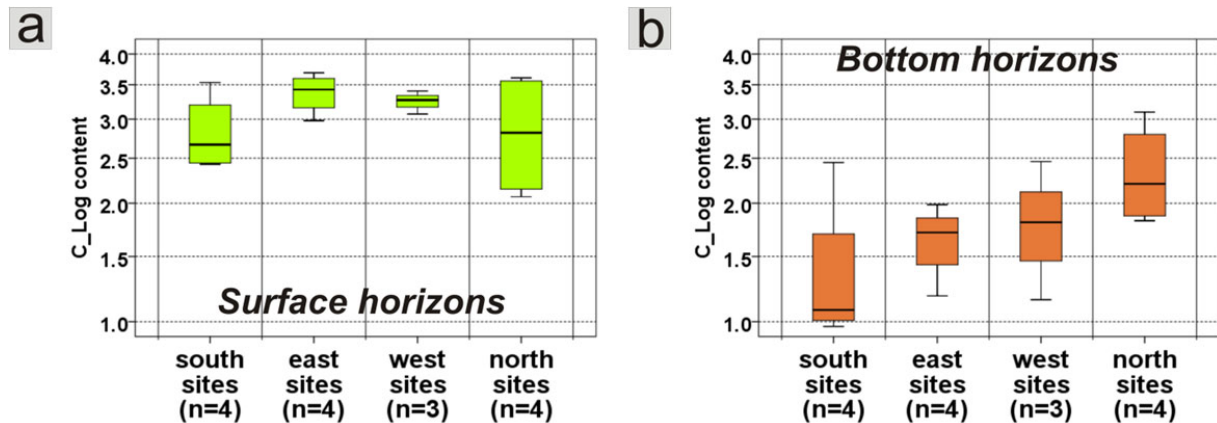


Figure 26: Boxplot comparison of carbon content in: (a) – surface soil horizons and (b) – bottom soil horizons of four study sites located around the town Tiksi. Note that values of carbon content were log transformed prior to plot.

Significant difference for total organic carbon (TOC) and nitrogen content in the surface horizons (non-parametric Mann-Whitney U test, $p < 0.05$) were found between all sites of the Tiksi area and the Lena River Delta region suggesting higher carbon and nitrogen contents in the hinterland area (Fig. 27). Study sites of the Lena River Delta also differed from the Tiksi area site by higher median values of pH, which is probably due to differences in geological setting between these two investigated areas.

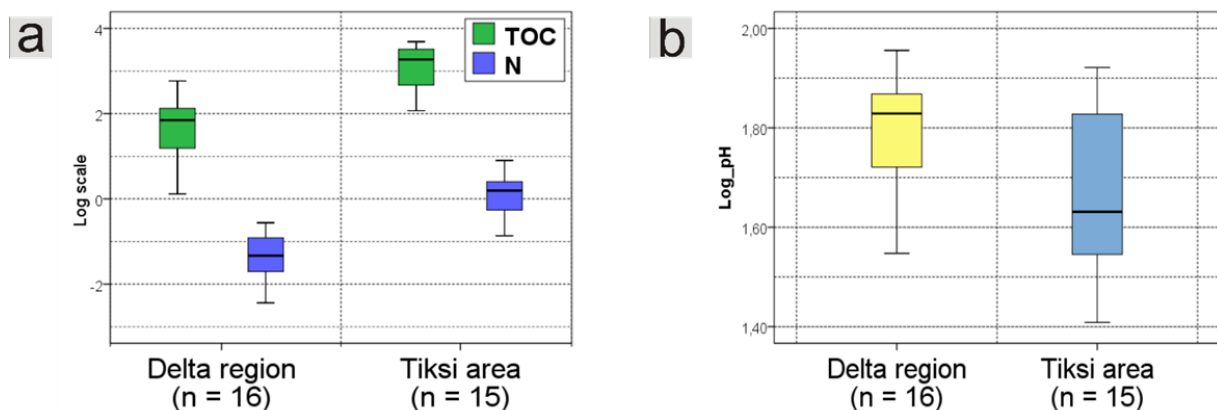


Figure 27: Boxplot comparison of carbon and nitrogen contents (in %), and pH values in investigation sites of the Lena River Delta region and the Tiksi area. Note that values for carbon and nitrogen contents and pH were log-transformed prior to plot.

5.2 Features of trace metal distribution in soils

5.2.1 Landscape distribution of trace metals in the Lena River Delta and its Hinterland

Results of trace element concentrations (median, minimum and maximum values) for all investigated geomorphological units are summarized in Appendix, Tab. V. The lowest median and minimum values of Fe, As, Cu, Ni, Pb, and Zn were found at the study site 2T-1 of the second terrace. The southernmost site H-3 of the north-south transect was characterized by the highest median values of Pb, Cu, and Zn. Geographical environments (vegetation cover, temperature and precipitation) might affect the soil formation and development processes and influence on element distribution within the soil profile of this studied area. High median concentrations of these elements were also observed in the units located on the first and the third terrace. The study sites of the third terrace were notably different from the other units by showing the highest median contents of Mn suggesting more advanced soil development processes. Cd content was under the detection limit for the study site of the third terrace (3T-2) whereas the highest median was detected for the study site H-1 of the hinterland area. All investigated sites were characterized by very low concentrations of Hg which were close to the detection limit.

The comparison of the results with studies reported for other northern regions (Appendix, Tab. VII) showed higher median values of Fe, As, Co and Zn concentrations for all our study sites except for study site of the second terrace (2T-1). Median contents of Mn for the units of the third terrace were higher than for Gleysols (FAO, 2006) reported by Salminen et al (2004). However, the range of Mn content in all investigated units coincided with the reported values of other studies. A wider range and higher medians of Ni, As, and Zn were comparable to the data reported by Rovinsky et al (1995) for Tundra Gleysols of the Lowest Lena River area. For study sites of the first terrace (site 1T-Ce1) and hinterland (site H-1), which were characterized by an accumulation of organic matter in their profiles, the median concentrations of Cu were higher than the values found for Histosols (FAO, 2006) of the Eastern Barents region (Salminen et al, 2004), and organic soil layers in Eastern Baltic region (Salminen et al, 2011). Because of limited geochemical data for the Siberian region, and despite different approaches of trace element extraction methodology, results were compared with the data given by Zhulidov et al (1997a,

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1997b). The maximum contents of Cu in the investigated units were lower than values reported for pristine wetlands of northeast Siberia. The maximum concentrations of Cd, Cu, Pb and Zn for all studied soils were much lower than the values reported for anthropogenically affected areas of western Siberia. The minimum concentrations of Cd coincide with the values reported for polygon bog peat of the background area in western Siberia (Appendix, Tab. VII, data source 5). However, the minimum contents of Cu, Pb, and Zn for all soil profiles except for studied site of the second terrace (2T-1) were higher than the data reported by Zhulidov et al (1997a). Concentrations for the majority of metal elements in soils of this study were similar to element levels in soils of remote areas in the Usa River Basin (Walker et al, 2003), and the Pechora River Basin, northeast European Russia (Walker et al, 2006a; Walker et al, 2006b; Walker et al, 2009). Resembling values for Cu, Hg, Mn, Pb, and Zn were found in soils of this study as well when compared to concentrations in pristine soils from the sub-Arctic region of Labrador, Canada (Walker, 2012).

Effects from human activity can be substantial in close vicinity to contamination sources (Jaffe et al, 1995; Zhulidov et al, 1997b; Ziganshin et al, 2011) but also remote from them (Thomas, 1992; Akeredolu et al, 1994). To detect presumable anthropogenic element additions to soil ecosystems, the ratio of trace elements in top and bottom soil horizons is used. However, as some studies show (Reimann et al, 2008; Sucharova et al, 2012) this technique cannot be beneficial in all cases. Usually the top layers are organic-rich and reflect the biogeochemical cycle at the earth surface. They differ significantly from the minerogenic layers which mainly reflect mineralogical developments during weathering, and, as in our investigation area, frost processes. In order to provide a clear idea of the vertical distribution of trace metals within the soil profiles of the north-south transect, the trace metal concentrations per soil volume in the top and bottom soil horizons were calculated (Fig. 28). In all cases, the bottom soil horizons contained slightly higher volumetric amounts of all measured trace elements in contrast to the top soils (except the element Cu for the study site 2T-1). This finding was most evident in Fe distribution for studied sites of the third terrace, first terrace (site 1T-1), and the hinterland (site H-3). The western side's valley belt along the Lena River between 72° and 67° N belongs to the so-called litho-chalcophile structural-formational complex (Geological Atlas of Russia, 1996). This area is characterized by high content of sulphide minerals (elements including Pb, Zn, Cu, Hg, and As) and by high element accumulation coefficients (R_k) which ranged from 2.5 to 5. These observations support the hypothesis of a geological origin for those trace elements at the

study sites. The volumetric concentrations of elements Ni, Cu, Co, and Pb in the top 1 cm layers found to be very close to the values observed for watersheds of the Yenisey River Delta area distant around 300 km far from the Norilsk mining industry (Korobova et al, 2003).

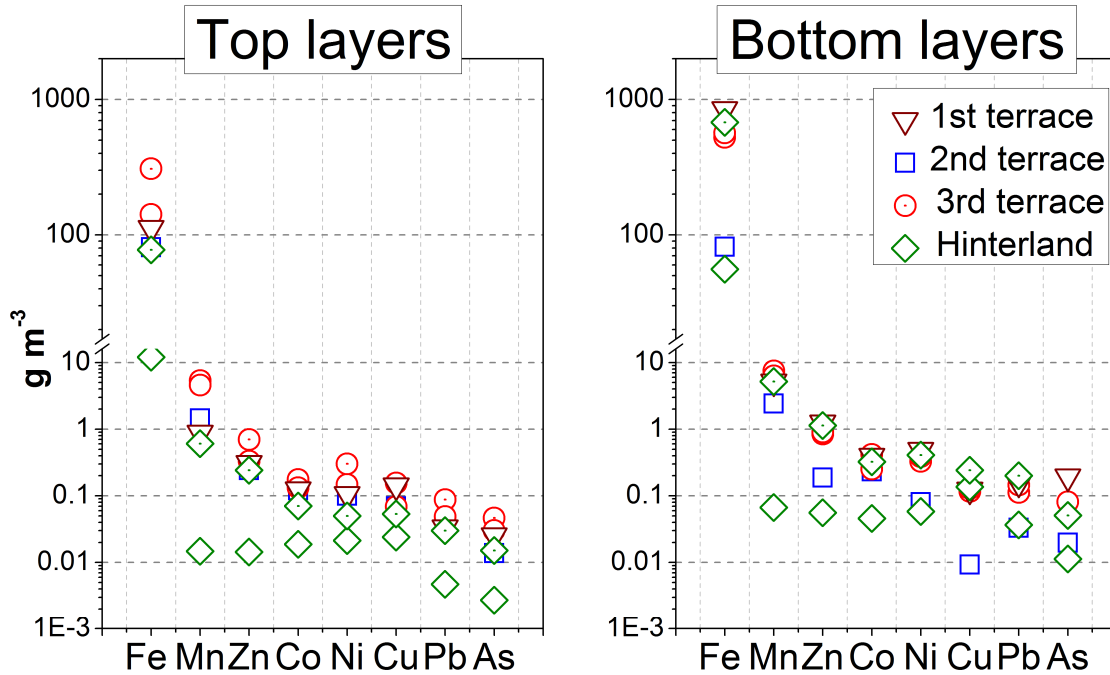


Figure 28: Volumetric concentrations of trace elements in 1 cm of top and bottom soil horizons of investigated sites of the north-south transect in northern Siberia ($g\ m^{-3}$). Symbols with centred dot point out the sites of the third terrace (3T-1) and the latitudinal transect (H-3), respectively.

5.2.1.1 Element distribution within the great soil groups

To reveal differences in trace elements distribution in studied soils, we combined the great soil groups for each of the determined soil suborders of the US Soil Taxonomy (Soil Survey Staff, 2010) according to the organic carbon content. Figure 29 shows a log-boxplot graph of the 10 trace elements distribution for each of the determined soil group. The first combined group which includes *Historthels* and *Fibristels* (Fig. 29a) with a higher organic matter content (up to 40 %) was characterized by higher medians and smaller ranges of values for Ni and Cu, and by a higher median value and bigger range of the Mn content. The second group shown in Figure 29b represents the soils of the *Aquorthels* and *Haplothels* with median carbon content of 8 %. In this group, the distribution of Fe was characterized by high variability similar as in the first group described above. However, the distribution of Co, Cu, and Cd concentrations had a wider range

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than the organic-rich soils. The third combined group including all kinds of Turbels with the median value of 2 % organic carbon was generally characterized by higher scatter of element contents except for Mn and especially Fe. A notably higher median value of Fe concentration was detected in the Turbels suborder. Comparison of the great soil groups of permafrost-affected soils investigated in this study showed some consistencies of the element distribution within these groups. However, the group division greatly depends on the soil properties of the studied soils. Thus, as it was also noted by [Baize \(2010\)](#), content and distribution of trace metals in soils does not depend on the soil name but on soil properties (organic matter content, chemical composition of parent material, soil texture and other important physical and chemical soil properties).

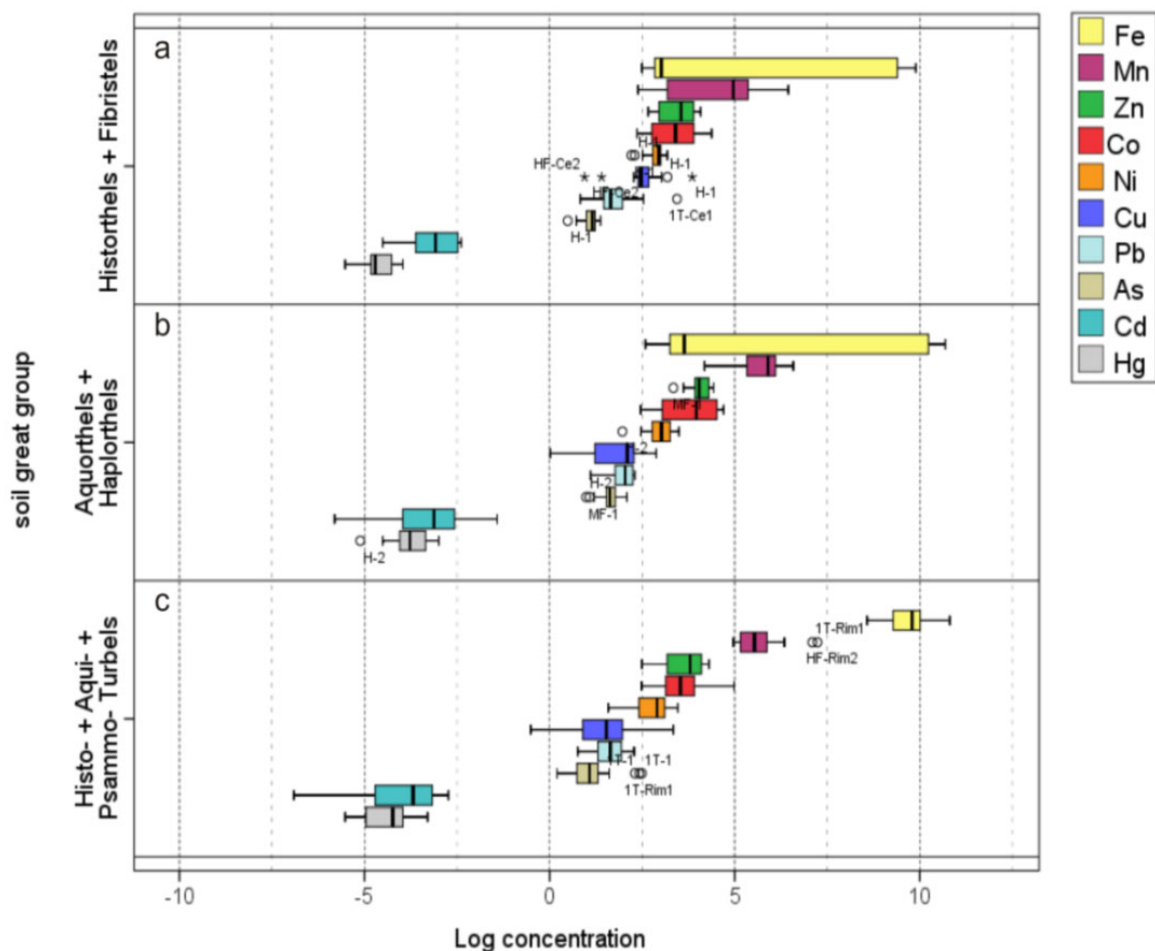


Figure 29: Log-boxplot comparison of gravimetric concentration levels (in mg kg^{-1}) and variations of 10 elements in soil great groups based on three soil suborders Turbels, Histels and Orthels. Note that concentrations for all elements were log-transformed prior to plot.

5.2.2 Distribution of trace metals in topographic units of Samoylov Island

The amount and distribution of iron oxides in soils are known to influence soil properties such as anion adsorption, surface charges, specific surface area, aggregate formation, nutrient transformation and pollutant retention in soils. In permafrost-affected soils, Fe is accumulated in the unfrozen soil horizons (Boike & Overduin, 1999; Fiedler et al, 2004), and is likely to be discharged with water during freezing and thawing processes to Fe-rich streams. Later, these processes might cause the mobilization of other elements and their further migration and accumulation within the active layer of the soil profile (Fiedler et al, 2004; Mahaney et al, 2010). The ratio of different Fe-oxide fractions can be used to evaluate environmental conditions and the processes of modern pedogenesis in permafrost-affected soils (Zonn, 1982; Zubrzycki et al, 2008). Higher values of the Fe-oxide ratio were found in the bottom part of the investigated profiles on Samoylov Island. This finding is probably related to less pronounced processes of pedogenesis due to the prevalence of anoxic conditions. The ratio between the so-called “active” Fe-oxide, the oxalate-soluble part - Fe_o , and well crystallized forms of Fe-oxides, the dithionite-soluble fraction - Fe_d , was higher in the bottom part of the polygon rim 1T-Rim1 (Fig. 30). This higher ratio could be explained by intensive mixing of mineralogical particles and organic compounds within the soil profile of the polygon rim due to cryoturbation. As a result, with the increase of the organic matter content within the sub-soil the amorphous forms of Fe-oxides (Fe_o) could form stable Fe-organic complexes.

The results comparing element levels within and between the soil profiles are displayed graphically by boxplots in Figure 31 using trace metal values from Appendix (Tab. V). The highest median values of Fe, Co, and As were found for the studied site of the middle floodplain (MF-1). Higher content of iron could be explained by additional input of allochthonous material during annual flooding. According to Adriano (1986), Co is an element that accumulates in the hydrous oxides of Fe, as well as As which usually has a tendency to form insoluble compounds with iron. The site of the middle floodplain was also characterized by higher variability of Fe, Zn, Ni and Cd. As the element Co, Zn and Ni are found to be easily adsorbed by Fe hydroxides (Salminen et al, 2004). An enrichment of the elements Mn, Fe, As, and Co at the cryoturbated polygon rim (site 1T-Rim1) was found in the layer of a distinct visible band of Fe accumulation. This accumulation was caused by element redistribution at the capillary fringe in these groundwater-affected soils (Fiedler et al, 2004).

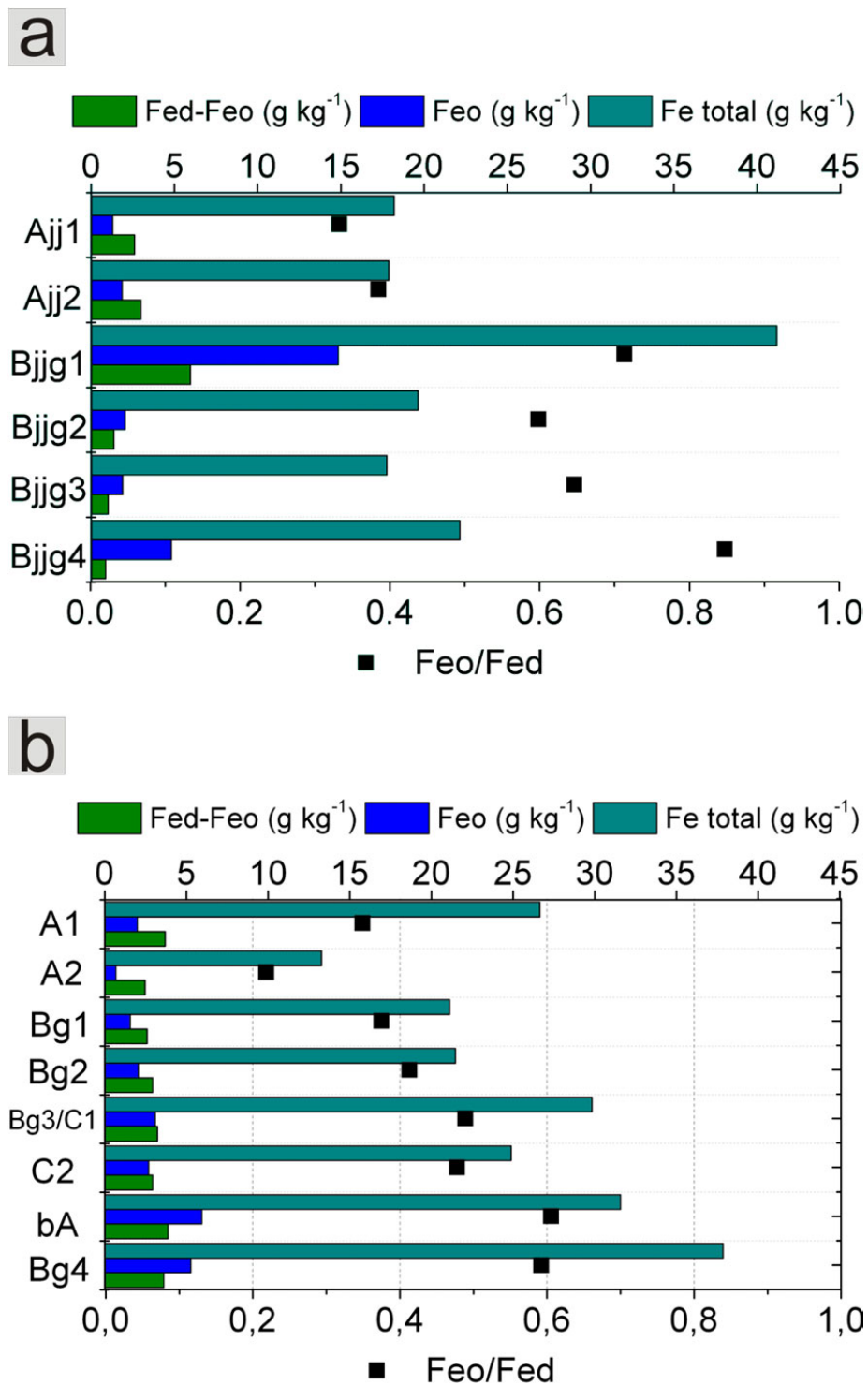


Figure 30: Vertical distribution of iron in soils of: (a) – polygon rim 1T-Rim1 of the ancient estuarine terrace and (b) – alluvial soils of the middle floodplain MF-1, where Fe_d is well crystallized forms of Fe-oxides, Fe_o is poorly crystallized forms of Fe-oxides, and Fe_{total} is amount of iron in soil extracted by aqua regia.

Detailed comparison of polygonal landscape micro-forms revealed differences in element distribution between the polygon rims and polygon centres. Higher median values and less variability of Mn content were found within the elevated part (site 1T-Rim1) of polygons in contrast to low-centred parts (site 1T-Ce1) of the first terrace polygon. Such a difference may be explained by redox and hydraulic gradient as described in detail by [Fiedler et al \(2004\)](#) (upward translocation). The maximum content of Mn was detected on studied site of the high floodplain (HF-Rim2) at a poorly elevated polygon rim. Manganese nodules found at the depth of 29-35 cm could indicate the occurrence of seasonal redox changes (precipitation of Mn ions as Mn hydro-/oxides with increasing oxygen level). It is interesting to note that the highest median content and the smallest range of Cu were observed for the most organic-rich soil of 1T-Ce1 belonging to the low-centred part of a polygon. It was shown in several studies ([Adriano, 1986](#); [Kabata-Pendias & Pendias, 2001](#)) that organic-enriched surface soil horizons contain higher concentrations of Cu than lower soil horizons which contain less organic matter. The investigated sites at the high and middle floodplains were characterized by a much higher range of Cu distribution within the profiles compared to the first terrace soil profiles. A smaller range of Cu in 1T-Rim1 soil profile was likely caused by more pronounced homogeneity (mixing of organic matter with mineralogical material) within the soil layers. The polygon centre 1T-Ce1 also differed from other sites by having a high median and the widest variability of Pb content. The maximum Pb content for this soil was observed in the sub-surface soil horizon. A clear-cut interpretation of this phenomenon cannot be provided, but different processes might cause this distribution: Pb compounds, found in soils are quit immobile ([Salminen et al, 2004](#)). However, some investigations showed that solubilization of Pb could be attributed to soluble chelate complex formation with organic matter ([Stevenson & Welch, 1979](#)). So the observed distribution of Pb might be caused by a combination of the dominant species (*Carex Aquatilis*, *Wahlenb.*) root uptake and downward movement as soluble chelate complexes with organic matter. Another reason might be the cumulative influence of seasonal freezing and thawing cycles and formation of ice lens ([Overduin & Young, 1997](#)). As a result, a solute is excluded from soil matrix and, due to convective water transport to the freezing front, accumulates in sub-surface soil horizons.

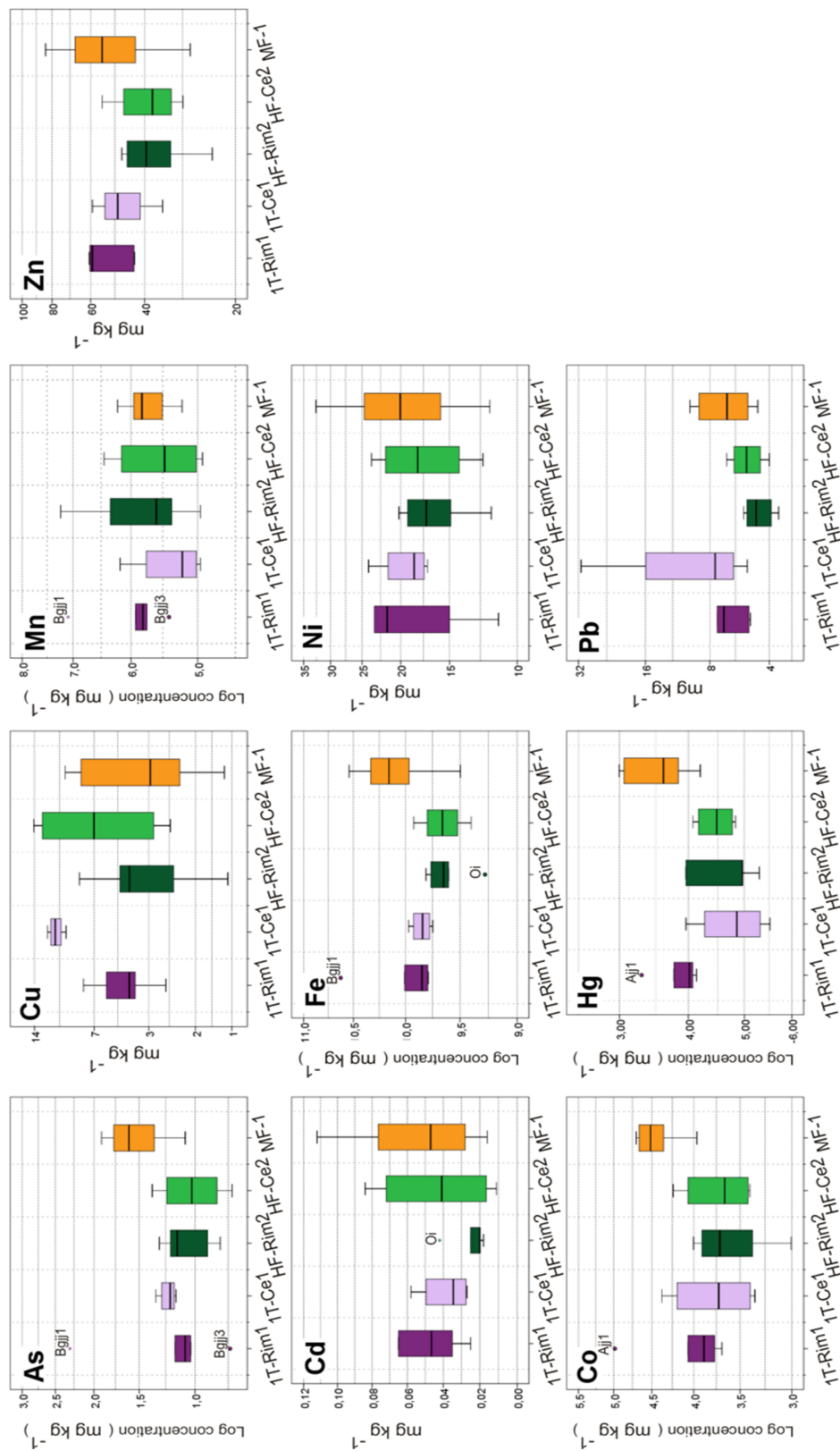


Figure 31: Boxplot comparison of element distribution (in mg kg^{-1}) in soils of Samoylov Island. Note that the values of As, Co, Fe, Hg, and Mn are log-transformed.

Relationships between the trace metal contents and soil properties were evaluated by means scatterplots (Reimann et al, 2008). Some selected examples of element distribution dependence from the observed soil characteristics are given in Figure 32. The elements As and Cu showed a tendency to associate with well crystallized Fe-oxide forms. Evans (1989) claimed that Cu has a stronger tendency to form associations with oxide forms of Fe, relative to other metals. It also holds true for the behaviour of As mediated by Fe-oxides presence (Adriano, 1986; Selim, 2011). A positive correlation of element concentrations with increasing organic matter content was found for the elements Cu (study sites MF-1, 1T-Rim1, 1T-Ce1) and Cd (sites MF-1 and 1T-Ce1). The elements Zn and Pb mainly coincided with clay content in soils. However, the role of insoluble organic materials (in case of polygon centre sites) and the oxides of Fe and Mn cannot be ignored. A tendency to positive correlation between Ni-Fe, Ni-Pb, Ni-Zn, and Ni-Cd was observed. The scatterplots for the last two couples of elements are shown in Figure 32d.

All investigated sites were characterized by a slight concentration increase of the majority of trace metal above the permafrost table in a gleyic layer. This was more pronounced for the elements Zn and Ni at the study site 1T-Rim1 and for Mn, Fe, and As in the soil profile of the middle floodplain MF-1. A similar trend for the distribution of elements was observed for peat cores of a Canadian peat (Chagué-Goff & Fyfe, 1997), permafrost-affected soils of tundra landscapes in the Yenisei River Delta (Korobova et al, 2003), and in soils of the polygonal tundra in northern Siberia (Fiedler et al, 2004). This similarity supports the suggestion that the presence of the permafrost table could cause this increase by acting as a geochemical barrier to further trace metal dislocation within the soil profile.

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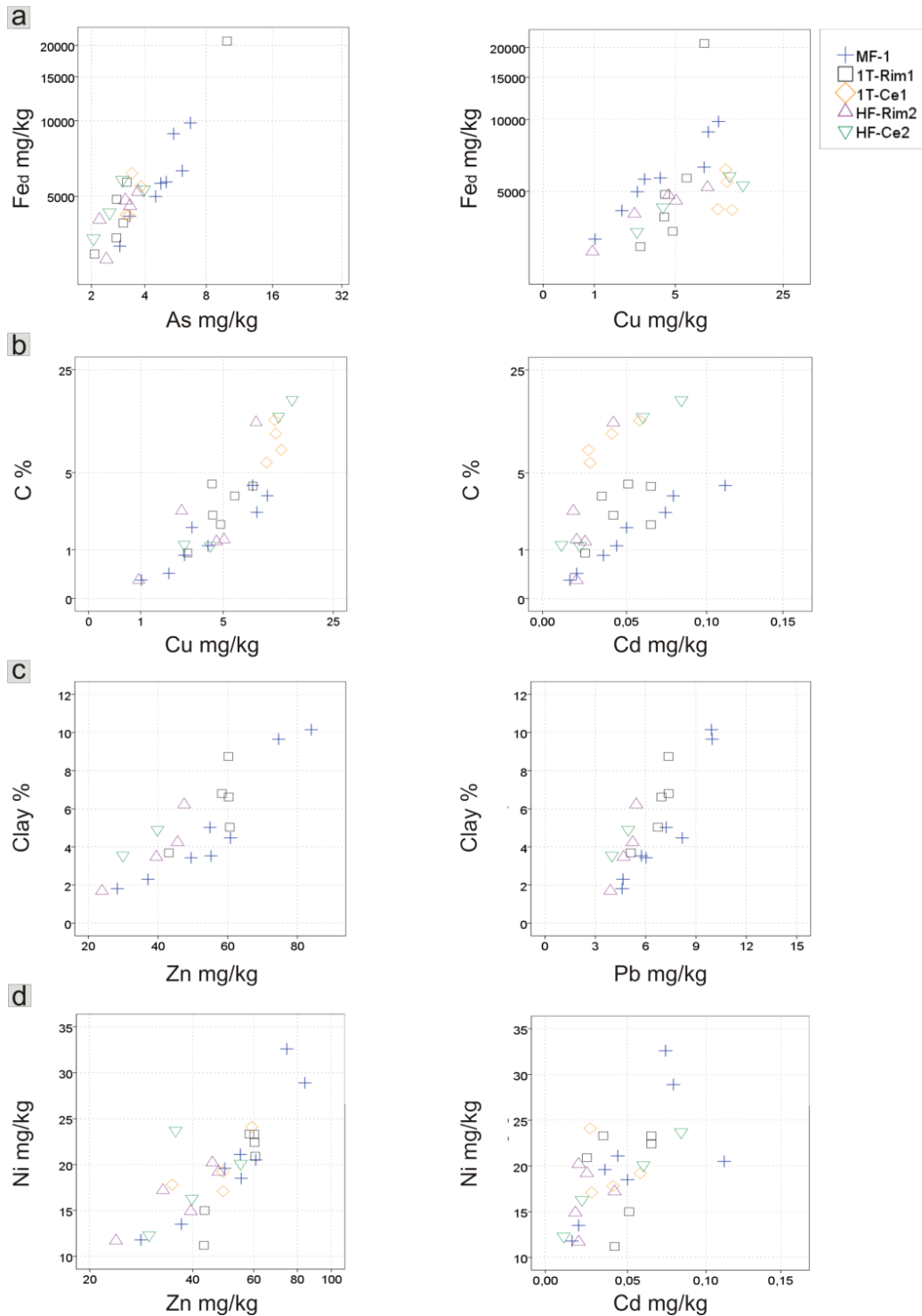


Figure 32: Scatterplots showing the interrelation between the selected elements and the general soil properties in the soil profiles of Samoylov Island: (a) – correlation between the elements and well crystallized form of Fe-oxide, (b) – the elements and organic carbon content, (c) – the elements and clay content, and (d) – correlation between the elements.

The vertical distribution of selected elements and some soil properties (pH and OM) in the soil profile 1T-d are shown in Figure 33. Maximum concentrations of Co and Cu were found in the surface soil horizon and amounted to 181 mg kg⁻¹ and 65 mg kg⁻¹, respectively. Cu concentrations for this study site were two times higher than for other sites located in different geomorphological units of Samoylov Island, although other elements (e.g. As, Cd, Fe, Pb, Mn, and Zn) were similar to the data obtained for other studied sites. Regardless of the fact that similar maximum values of Cu were found in hydric soils, and sedge-moss peats of northeast Siberia investigated by [Zhulidov et al \(1997a\)](#), the content of this element in the surface soils (0-10 cm) of Samoylov Island (n=7) were considerably less than the values for the 1T-d study site (Fig. 34). The concentrations of Cu in 1T-d surface soils were nearly two times higher than the average background concentrations of this element in peat soils of Germany ([LABO, 2003](#)). Evaluated total organic carbon (TOC) in the surface layers of 1T-d soil core probably reflects not only the inclusion of the vegetation but an occurrence of diesel fuel products on the surface. Additional input of Cu on the surface together with residuals of Cu-contained material (e.g. wires) led to the accumulation of Cu in the surface soil horizons. Thus, elevated organic matter content and acidic soil reaction possibly governed the intensive accumulation of Cu in the sub-surface soil horizons of 1T-d study site. With pH values increase in subsurface horizons, Cu likely migrated downwards being a part of fulvic and humic acid compounds ([Kovalskiy & Andrianova, 1970](#)).

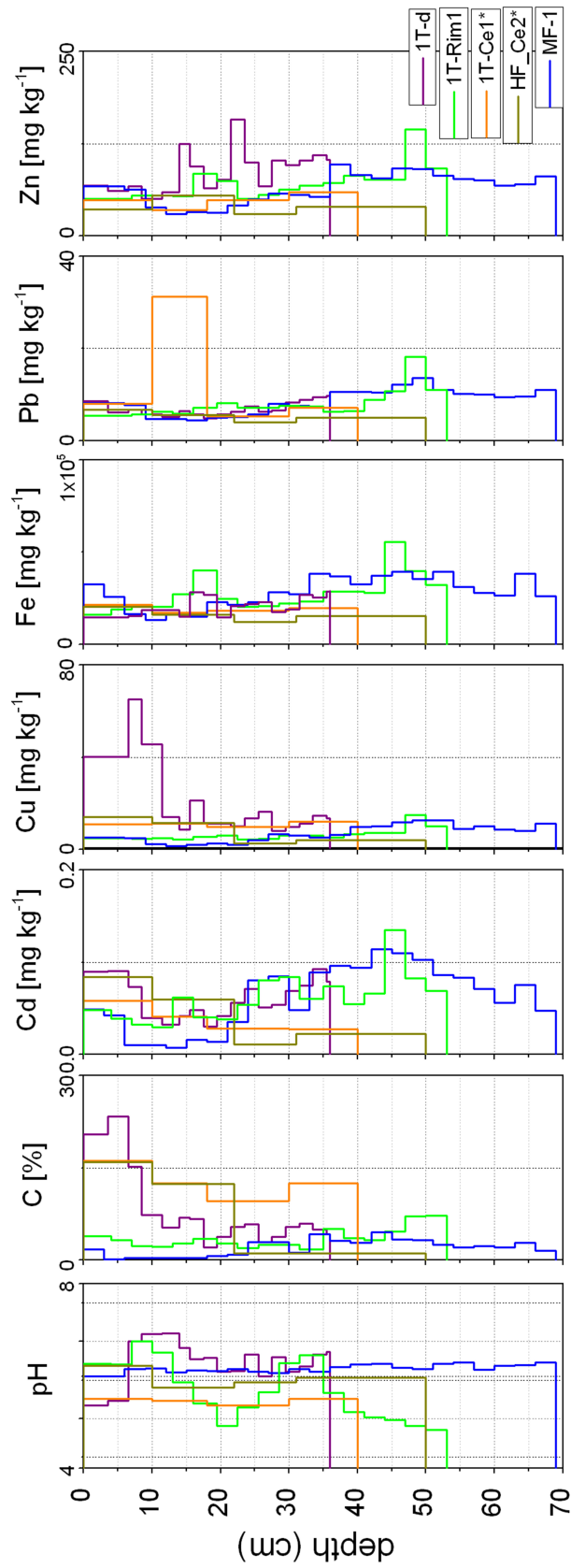


Figure 33: Vertical distribution of pH, organic carbon (OC), and selected trace metals in the soil of 1T-d of Samoylov Island investigated in 2009. The soil profiles of the sites investigated in 2010 were plotted for the comparison.

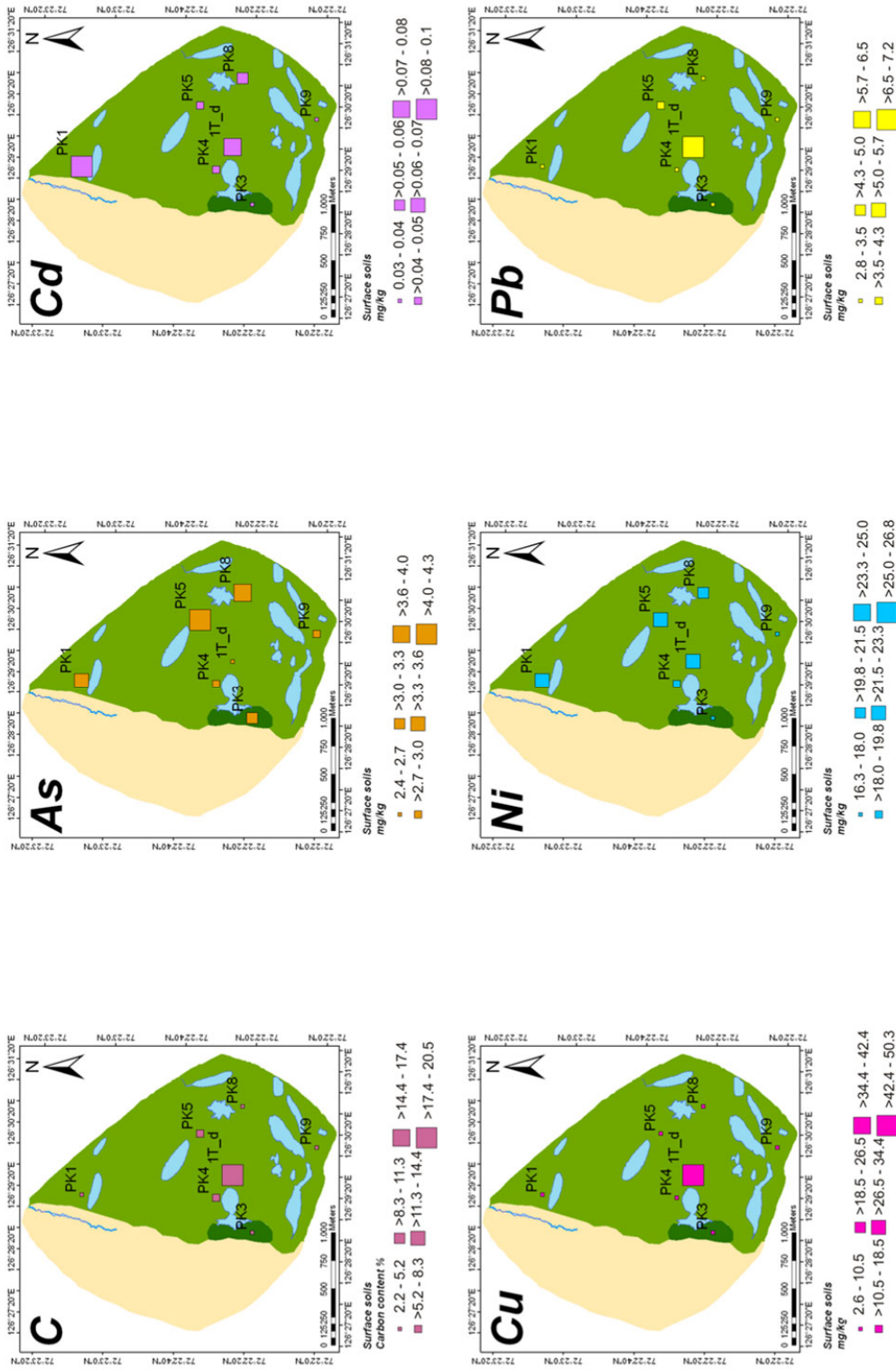


Figure 34: A map of Samoylov Island showing selected element concentrations in the surface soils (0 – 10 cm) and indicate the notably higher carbon content C (in %) and concentrations of Cu and Pb (in mg kg⁻¹) for the study site 1T-d on the former placement of the EDDY covariance station in comparison with other surface soils located in the first terrace of Samoylov Island.

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5.2.3 Trace metal distribution in soils of Tiksi area

Element concentrations (median, minimum and maximum values) for all study sites around the settlement Tiksi are shown in Appendix, Tab. VI. The highest median concentrations for Cd, Co, and Cu were observed in soils of the eastern site (TH15). The western sites differed significantly from eastern and northern sites by higher median concentration of Ni in the surface soils (Fig. 35). Southern sites, which are remote from the town Tiksi, were characterized by a scatter of Ni content. The highest median concentration of Ni, but low median values for Cd and Cu were found at TH1 study site. High median contents for Zn were found in soil profiles of eastern site, whereas its low median values were detected for soil profiles of the northern site. The maximum concentration of Pb was found at TH9 study site in the surface horizon when compared to the concentrations in surface soil horizons at all other studied sites.

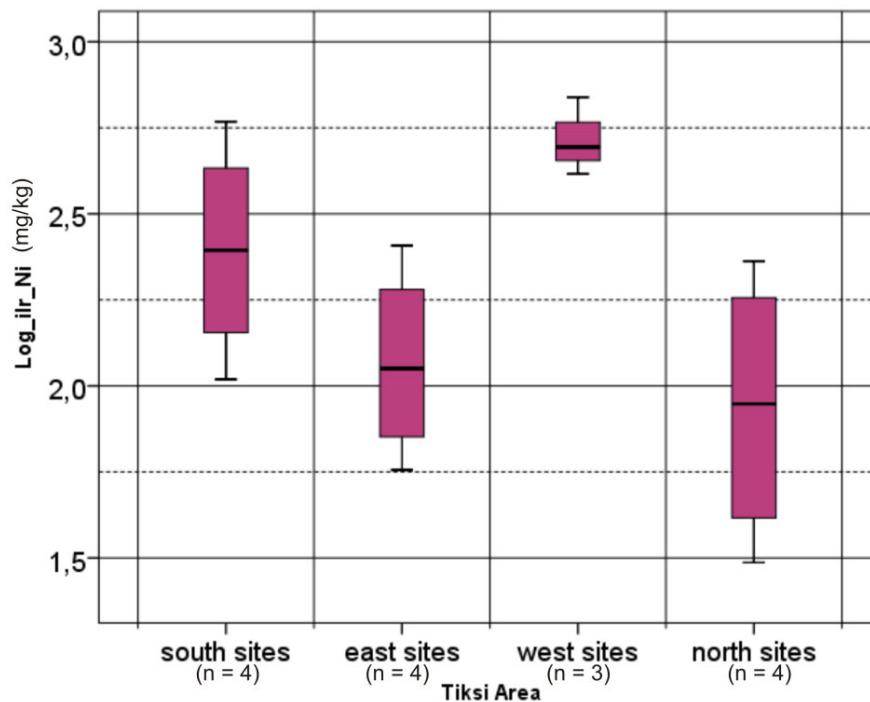


Figure 35: Boxplot comparison of Ni content at four studied sites of the Tiksi area. Note that the values of Ni are log-transformed.

Stratigraphic plots of base soil characteristics with selected element concentrations of the soil profiles at western and northern sites are given in Figure 36 and Figure 37, respectively.

Generally, western and northern sites differed from southern and eastern sites by higher abundance of Cd in the surface soil horizons. The western site which is represented by TH3, TH4, and TH5 forms a system of geochemically associated landscapes. They were described as upper slope, downslope, and depression site, respectively. It is interesting to note that within the confines of this associated landscape a consistency in some element distribution was observed. With increasing soil depth the organic carbon content gradually decreased in all three observed soil profiles. The vertical distribution of Cd, Cu, and Ni concentrations within the soil profiles TH3, TH4, and TH5 also had resembling features. Moving down the hill from the site TH3 to the TH5 through the site TH4, concentrations of Cd, Cu, and Ni in the surface horizons being the highest for the upper slope (TH3) were less in the surface soils of the downslope TH4 and far less in the surface soils of the depression site TH5. The opposite distribution of these elements was observed for the bottom horizons. Cd, Cu, and Ni formed the following order of their distribution in bottom horizons: TH5 > TH4 > TH3.

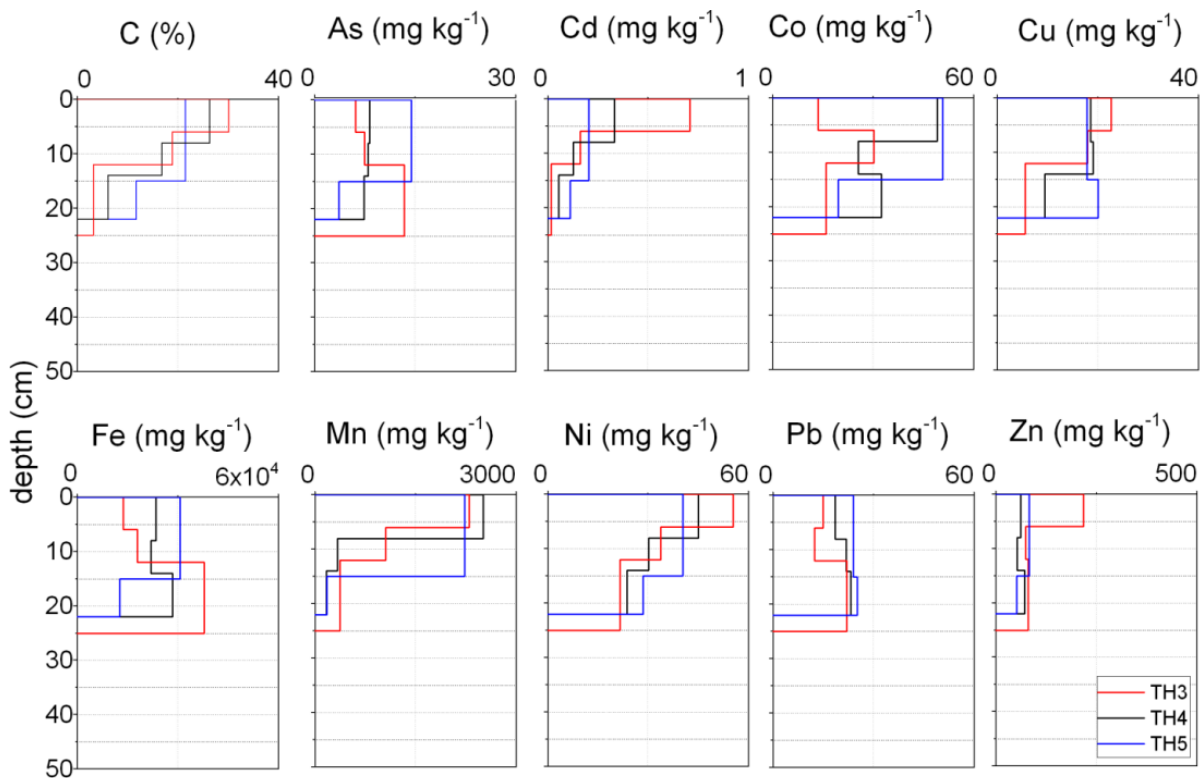


Figure 36: Stratigraphic plots at each of three sites on the western direction from the settlement Tiksi. The carbon content is expressed in %; the element concentrations are expressed in mg kg⁻¹.

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In contrast to TH4 and TH5 studied sites, the soil profile of TH3 site located on the upper slope was characterized by the maximum concentrations of Cd, Cu, Ni, and, Zn as well as the maximum carbon content in the surface layer. This observation may suggest strong association of all these elements with organic matter and as a consequence, the formation of chelate complexes in the surface soil horizon. Different behavior of As and Fe was observed for this landscape facie. Low concentrations for As and Fe were observed in the surface horizon of the site TH3. At the same time, the element concentrations in the surface horizons of the depressed site TH5 were the highest. The values of As and Fe for the site TH4 were intermediated between the values for TH3 and TH5. Accumulation of As and Fe occurred more intensively in bottom horizons of the upper slope TH3 than in bottom layers of the sites TH4 and TH5. Comparatively lower acidic nature in the surface horizons of TH3 and TH4 soil profiles in comparison with B-horizons were likely the main cause of the leaching of Fe and associated with it As into the underlying soil horizons and their further lateral downslope migration to adjacent forms of a landscape.

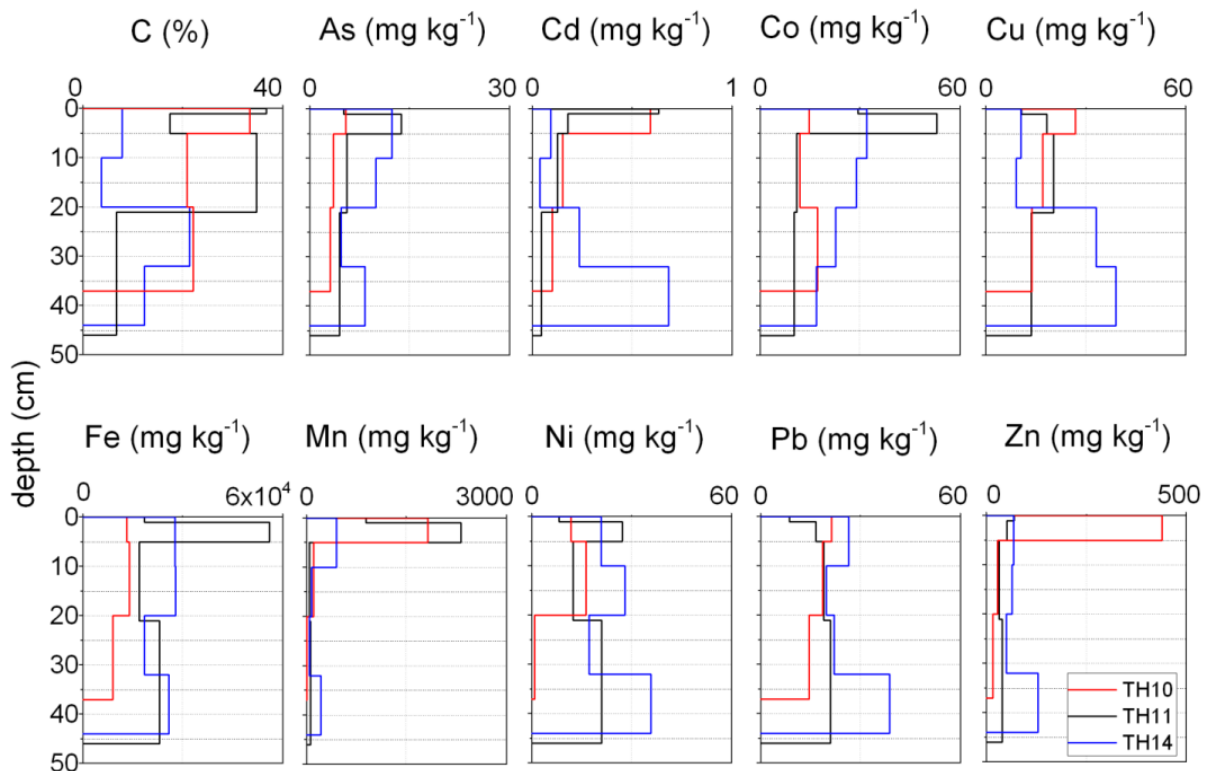


Figure 37: Stratigraphic plots of three sites on the northern direction from the settlement Tiksi. The carbon content is expressed in %; the element concentrations are expressed in mg kg⁻¹.

The site TH10, which is located to the north from the settlement, notably differed from all other soil profiles by the lowest abundance of the majority of metals such as Fe, Mn, Ni, and Zn in the bottom horizon *BCjj* (Fig. 37). However, the maximum concentrations of Cd, Cu, Pb, as well as Mn and Zn were found for the surface soil horizon *Oie* which was characterized by a higher soil pH in comparison with the sub-surface soil horizons. The accumulation of these elements was likely caused by the formation of so-called alkaline barrier which was formed at the surface horizon. The maximum concentration of Zn amounted to 440 mg kg^{-1} and greatly exceeded the values which were found for all other investigated sites around Tiksi (Fig. 38). The micro- and meso-relief of the study site TH10 (i.e. the elevated rim surrounded by argillaceous schist) ranges from east and west and the dominant seasonal wind directions suggested that the abundance of Zn may be due to aerial transport of dust particles from the mining operations located 600 m south-east right of TH10. Although this elevated concentration of Zn exceeded the maximum values reported for organic layer soils in Eastern Baltic region (total extraction) (Salminen et al, 2011) (Appendix, Tab. VIITable VII), for hydric soils in the northeast Siberia (Zhulidov et al, 1997a), and the average Zn concentrations reported for peat soil in Germany (LABO, 2003), it was still two times less the maximum concentrations reported for the areas of the western Siberia affected by anthropogenic pollution (Zhulidov et al, 1997b). The study site TH14 notably differed from the investigated sites of northern direction by features of vertical distribution for Cd, Cu, Pb, Ni, and Zn. High concentrations of these elements were observed in the bottom soil B-horizons, whereas in other soils of the Tiksi area the highest values for these metals were found in the surface soil layers. Concentrations of Cd, Cu, and Pb, abundance of which is usually associated with higher amounts of organic matter, gradually increased with increasing depth (Fig. 37). The maximum values of Cd, Cu, and Pb were found for the *Bhsjj* soil horizon of TH14 site which was characterized by the lowest pH value and the maximum organic carbon content. These concentrations amounted to 0.68 mg kg^{-1} for Cd, 39.0 mg kg^{-1} for Cu, and 38.9 mg kg^{-1} for Pb, respectively. The maximum concentrations of these elements did not exceed the maximum values reported for the hydric soils of the northeast Siberia (Zhulidov et al, 1997a), but were higher than the maximum values of these metals of in C-horizons of the southern Norway (Reimann et al, 2009) and average background concentrations in the German peat-formed bottom soil horizons (LABO, 2003). The values of Cu reported for the Lower Lena River area (Rovinsky et al, 1995) were six times smaller than the concentrations presented for this study site. The study site TH14 was located in immediate neighbourhood of the Bulunkan Gulf

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probably could be affected by intermittent inundations, and as a consequence – polluting agent input. It is entirely possible a mechanical impact on this area in the past.

Differences in the element content were found for various relief forms (depressions, slopes, and elevations). The coefficient of buffer capacity (*Bf*) for the surface soils showed that the majority of elements (Cd, Co, Cu, Mn, Ni, and Zn) accumulated in depressions (*Bf* is *high* and *very high*). The hill slopes of the study area were characterized by a *middle-to-high* coefficient of *Bf* for Cd and Mn, and low for As, Cu, and Pb. *Low-to-very low* coefficients of buffer soil capacity were found for Cu, Pb, Ni, and Zn in elevated parts of a relief. Based on these results, it could be concluded that Fe, Mn, Zn, and Cd migrate more actively in geochemically adjacent landscapes (Fig. 39). Thus, Fe could be leached out from soils of eluvial and downslope facies (Glazovskaya, 1988) and precipitate on oxic barriers of soils developed in depressions (superaqual landscapes). Mn and Co had similar behaviour in lateral distribution in geochemically associated landscapes. Lateral distribution of Zn was not uniquely defined. Possibly in autonomous landscapes, Zn actively leached from soils which contained less organic matter. Therefore, higher Zn concentrations were found mainly in depressed landscape forms. In cases when soils were developed on plane and poorly drained terrain, higher Zn concentrations could be found in the top horizons of these soils with higher content of organic matter. Zn is capable to form stable organic complexes. However, it is not usually included to humus compounds being mainly associated with oxides (e.g. Mn hydr/oxides). Increased concentrations of Pb, Cu, and Cd were observed in depressed relief forms, which is likely due to organic matter accumulation linked with an occurrence of acidic environmental soil conditions in the depression in the most of cases.

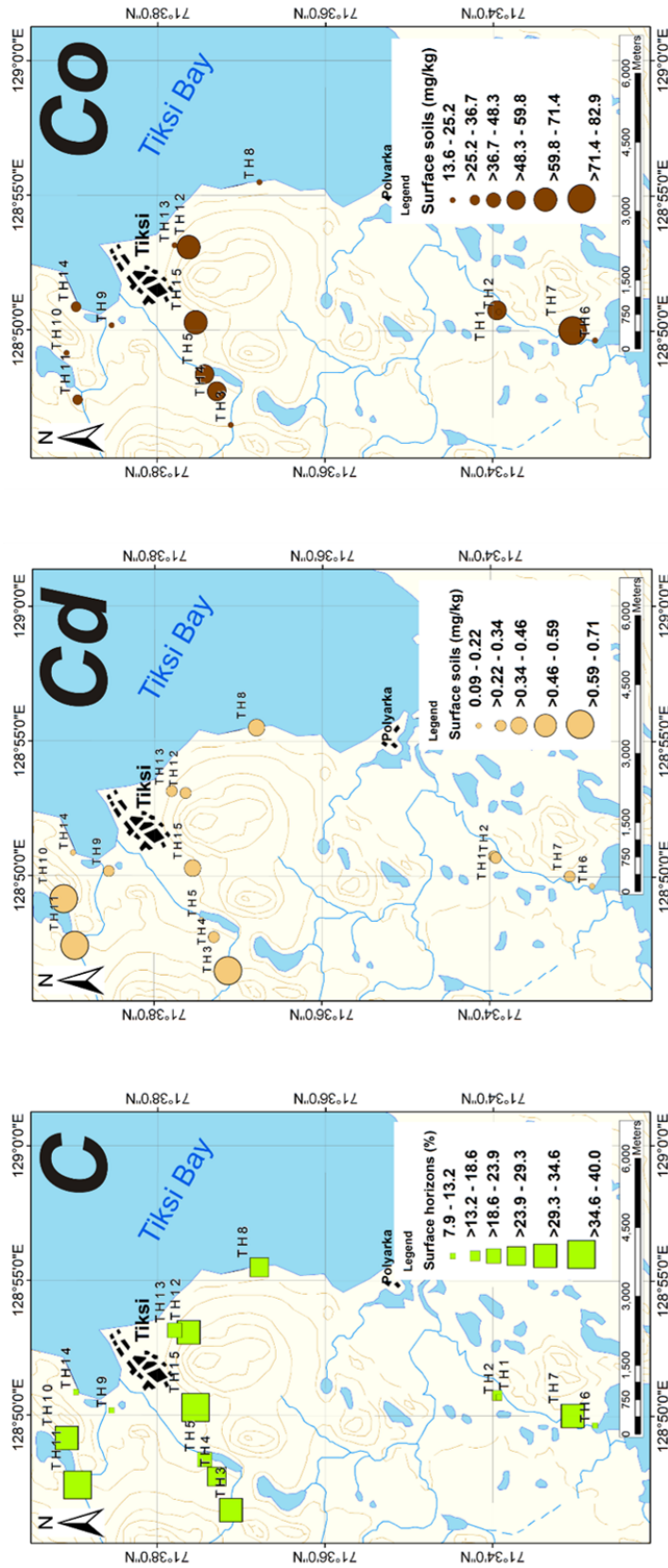


Figure 38: A map of an area near the settlement Tiksi showing the distribution of selected elements in 15 surface soil horizons. Carbon content is expressed in %; metal concentrations are expressed in mg kg^{-1} .

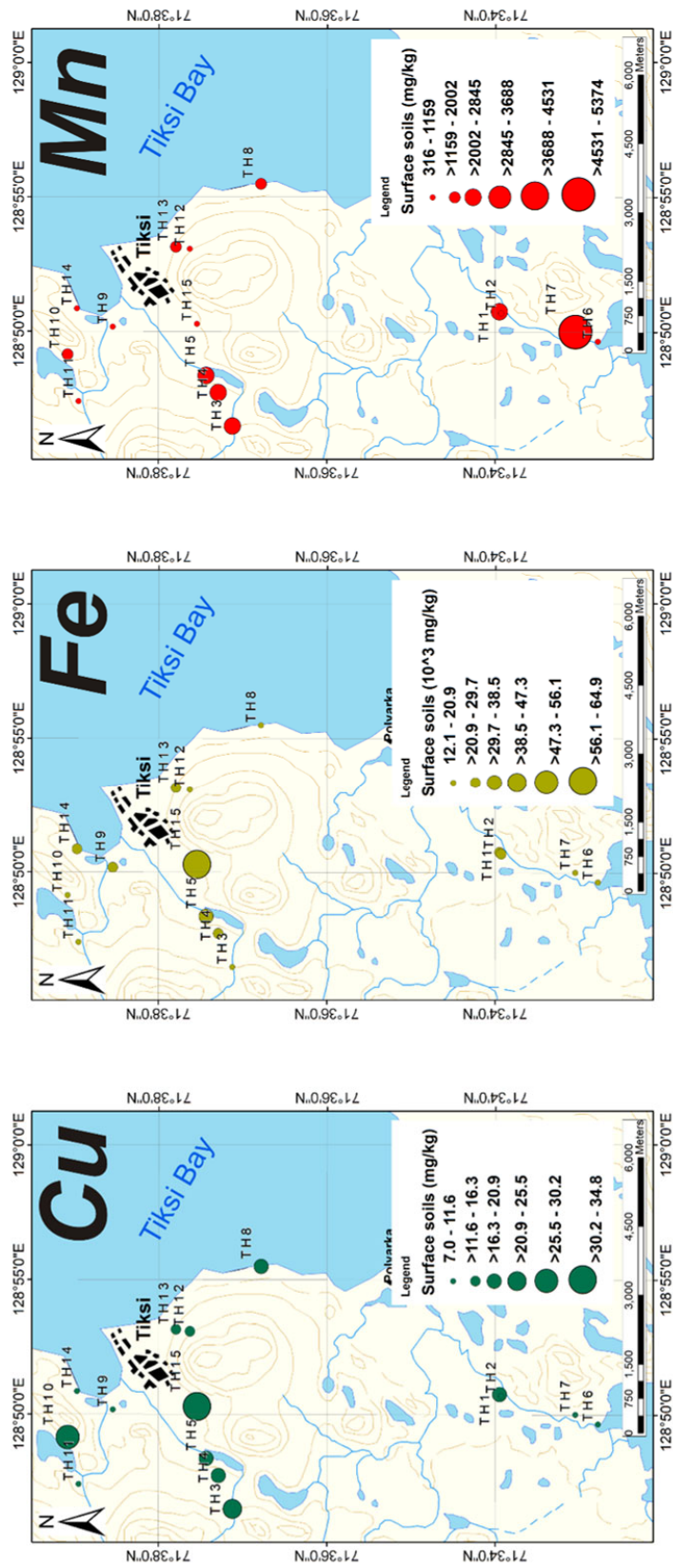


Figure 38: Continued.

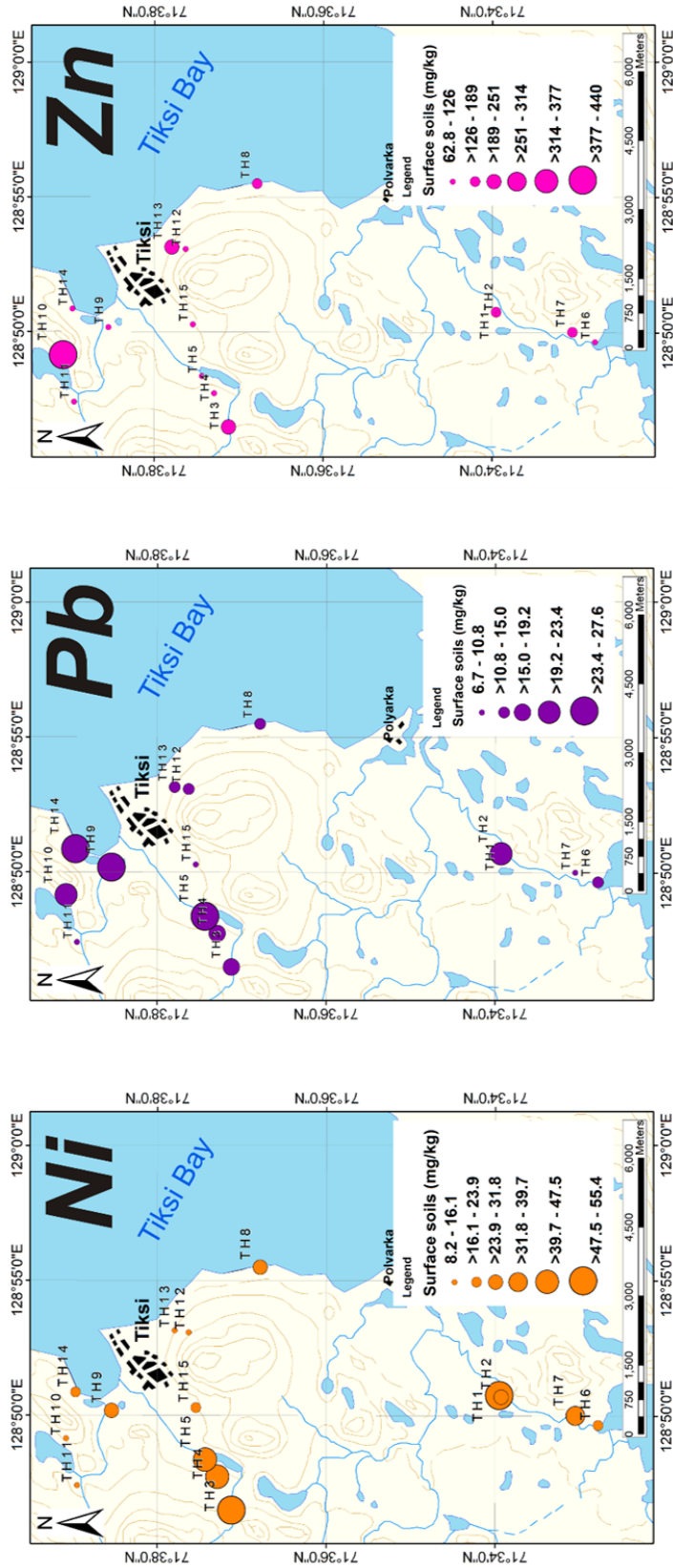


Figure 38: Continued.

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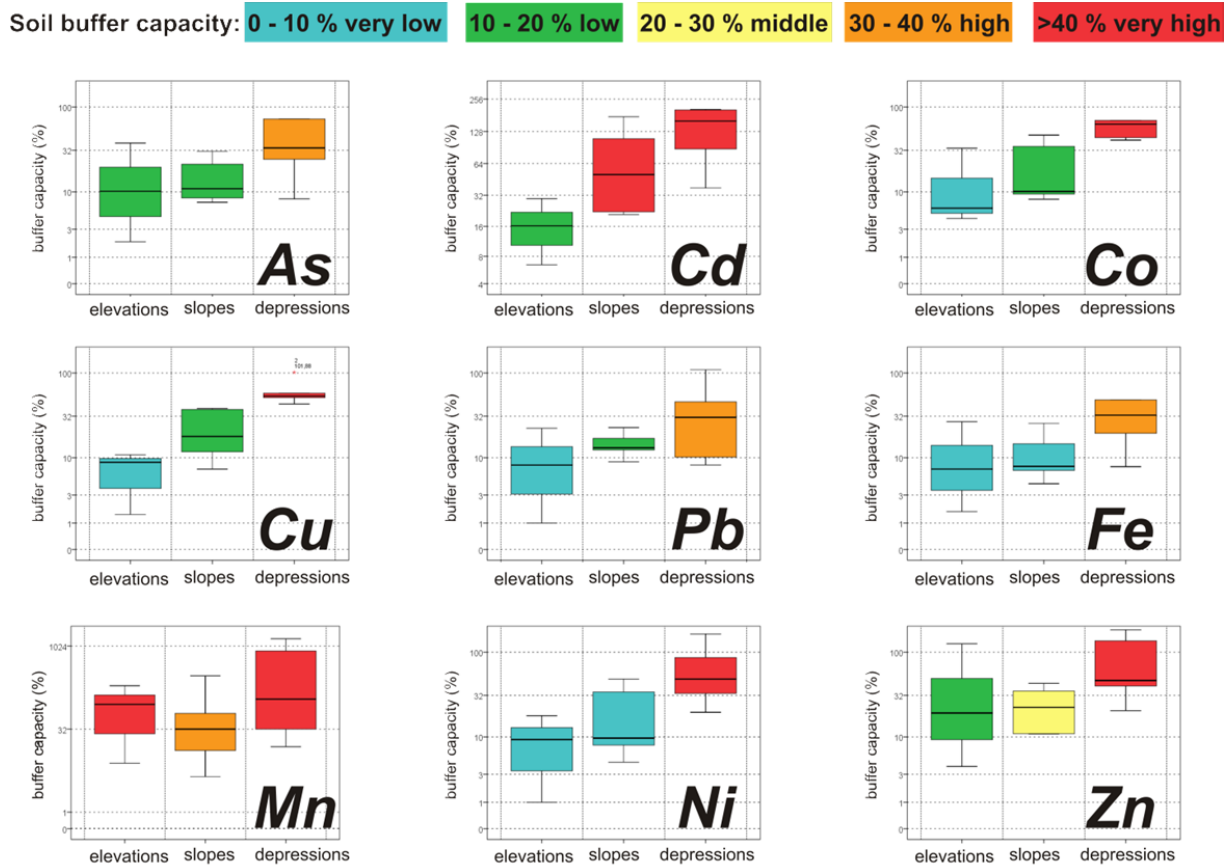


Figure 39: Coefficients of soil buffer capacity (B_f) for trace metals in the surface soil horizons of soils around the town Tiksi developed on elevated landscape forms, hill slopes, and depressions.

Statistical comparison the soil data of the Tiksi area and the Lena River Delta region is shown in Table 8. Compared to the Lena River Delta region, the surface horizons of the Tiksi area were generally higher in As, Cd, Cu, Mn, and Pb. No significant differences between the study regions were found for Co, Fe, and Ni in their abundance in the surface horizons. B-horizons of the Tiksi area differed significantly from the same pattern of the Lena River Delta area by higher concentrations of most elements (As, Cd, Cu, Ni, Pb, and Zn). No significant difference between two investigated regions in Fe and Mn abundance in B-horizons was found. Significantly higher concentrations of Co were observed for the B-horizons of the Lena River delta when compared with the Tiksi area. Differences in soil chemistry of these two investigated areas indicate the diversity of their landscape geochemical structures and therefore the mechanisms of element distribution in studied soils.

Table 8: Statistical comparison of soil data of the surface and bottom soil horizons in the Tiksi area to similar data obtained from the Lena River Delta (non-parametric Mann-Whitney U test). The name of a particular region indicated on the table suggests the occurrence of significantly higher metal concentrations found for a particular soil horizon.

Element	Surface horizons	B-horizons
As	Tiksi*	Tiksi*
Cd	Tiksi*	Tiksi*
Co	NS	Delta*
Cu	Tiksi*	Tiksi*
Fe	NS	NS
Mn	Tiksi*	NS
Ni	NS	Tiksi*
Pb	Tiksi*	Tiksi*
Zn	Tiksi*	Tiksi*

* $p < 0.05$

NS, not significant

Spearman's rank correlation analysis between the elements and base soil properties (pH and OC) for the soil layers of the Lena River Delta region and the Tiksi area is shown in Table 9. Positive correlation in the surface soils of both study areas was observed between Cu and organic carbon content, Ni and Mn. Positive correlation with As were shown for Fe and Pb. Negative correlations with OC content occurred for As, Fe, and Pb. Positive correlations with carbon content were observed for both study areas for Cu and Cd suggesting a strong relationship of these metals with organic-rich material. Negative correlations with Cu occurred for As and Fe in B-horizons of the Tiksi area in contrast to the mineralogical soil horizons of the Lena River Delta region, where the correlations between these elements were positive. Positive correlation with pH and Mn was shown for the Tiksi area indicating the dependence of this element from the changes of environmental soil conditions. Many elements showed more interactions to each other in B-horizons of the Lena River Delta region soils when compared with the underlying horizons of the Tiksi area. The area of the Lena River Delta is comparatively flat in contrast to the Tiksi area which, as a periphery of the Verkhoyansk, is characterized by relatively high altitudes mountain system. Regardless of the fact that soils of both investigated areas developed primarily in reducing conditions, the soils of the deltaic area were considerably more waterlogged. These conditions resulted in dominance of amorphous Fe forms which are strongly related with the organic matter, and as a consequence, the strong relationship with other metals occurs. The topographic features in the Tiksi area favoured more intensive development of reducing conditions in the depressions due to downward water drainage. One might assume that

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also more acidic soil conditions likely favoured more intensive element migration capacity in the mineralogical soils of the Tiksi area and binding some of them with fine-grained soil particles (loam or clay).

Table 9: Selected significant Spearman's rank correlation coefficients (r) between trace elements, soil OC, and soil pH in the surface and B-horizons of studied soils in the Lena River Delta region and the Tiksi area.

Components	r	Components	r	Components	r	Components	R
Surface horizons							
<i>The Lena River Delta n = 16</i>							
Pb – Cu	0.66**	Pb – Fe	0.62*	Pb – As	0.60*	Pb – Mn	0.53*
Ni – As	0.72**	Ni – Mn	0.69**	Ni – Fe	0.58*		
Zn – Fe	0.70**	Zn – Ni	0.62*	Zn – As	0.53*		
C – Cu	0.84**						
Fe – As	0.71**						
<i>Tiksi area n = 15</i>							
C – Cd	0.72**	C – As	-0.90**	C – Fe	-0.70**	C – Cu	0.53*
As – Fe	0.82**	As – Cd	-0.71**	As – Pb	0.62*		
Ni – Mn	0.61*						
Cd – Cu	0.59*						
Pb – C	-0.58*						
B - horizons							
<i>The Lena River Delta n = 21</i>							
Pb – Ni	0.98**	Pb – Zn	0.96**	Pb – Fe	0.91**	Pb – Cu	0.87**
Fe – As	0.95**	Fe – Ni	0.91**	Fe – Cu	0.80**	Fe – C	0.56**
Zn – Ni	0.95**	Zn – Fe	0.85**	Zn – As	0.80**	Zn – Cu	0.80**
C – Cu	0.87**	C – Pb	0.63**	C – Zn	0.59**	C – Cd	0.56**
As – Pb	0.85**	As – Ni	0.84**	As – Cu	0.77**		
Mn – As	0.56**	Mn – Pb	0.56**				
Ni – Cu	0.83**						
<i>Tiksi area n = 18</i>							
C – Cu	0.80**	C – Cd	0.74**	C – Fe	-0.76**		
Mn – pH	0.74**	Mn – Zn	0.69**				
Cu – Cd	0.76**	Cu – As	-0.71**				
Fe – As	0.71**	Fe – Cu	-0.71**				

** p < 0.01

* p < 0.05

The data obtained for O-horizons of this study was compared with the data reported for pristine soils of Labrador, Canada (Walker, 2012), and southern Norway (Reimann et al, 2009) (Appendix, Tab. VII). Median concentrations for the majority of elements (As, Co, Cu, Fe, Mn, Ni, and Zn) exceeded the values of background soil data reported by the above studies. Median concentrations of Cu, Pb, and Zn in the surface soil horizons around the settlement Tiksi were higher than the values for these metals in O-horizons reported for the Usa River Basin and

Pechora River Basin, and northeast European Russia (Walker et al, 2006a; Walker et al, 2006b; Walker et al, 2009), although the median contents of Cd and Pb were notably less when compared with the soil data reported by Reimann et al (2009). Chemical data from all investigation sites of the Lena River Delta region, its hinterland, and the Tiksi area were compared with the Approximate Permissible concentrations (Hygienic standards, 2009; Tab. 2, Section 2.1.3). The investigated soils of the Tiksi area with required properties (silt, loam, and silty clay with pH values less than 5.5) and soils of the Lena River Delta region with required properties (sandy loam with pH values more than 5.5) were characterized by smaller concentration values for all elements except for As in soils of the Tiksi area when compared with the approximate permissible levels in soils of sandy loam and clay texture with pH < 5.5. Comparison of the element concentrations in the surface soils of this study with the average background element concentrations determined for the peat soils of Germany (Tab. 3, Subsection 2.1.3) showed smaller concentrations of Cd, Cu, and Pb but higher contents of Ni and Zn for the Lena River Delta region and the Tiksi area. The concentrations of Cd, Cu (except for TH15), Fe, Mn (except for TH10), Pb, Ni, and Zn in the top soil horizons of all studied sites around the Tiksi area were much smaller than the metal contents in the top soils of the Khatanga area in northern Siberia (72° N, 102° E) reported by Negoită & Ropotă (2000). The variability of chemical composition of soils of the Tiksi area can be explained by a particular composition of underlying deposits (clay shale), roughness of the landscape, and prevalence of acidic and reducing soil conditions. It can unlikely be related to pollution caused by long-range atmospheric transport, as for the majority of the Arctic regions in Russia (Goryachkin et al, 1998; Glazov et al, 2006).

5.3 Features of chemical composition of plants

5.3.1 Element composition of plant species of the Lena River Delta Region

The collected vegetation species were present at all study sites of the Lena River Delta and covered more than 50 % of the area. The trace metal median contents notably differed among vegetation groups of the Lena River Delta (Appendix, Tab. VIII). The highest median concentrations of Cu, Fe, Ni, and Pb were found for mosses, whereas the lowest median values of Fe, Ni, and Pb were observed in shrubs. The lowest median values of Mn were found in lichen species. Significant differences in Fe, Mn, Ni, and Pb concentrations were found between mosses

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and lichens (non-parametric Mann-Whitney U test, $p < 0.05$). This finding suggests that these plant species have different behaviour in the element uptake with respect to these compounds, especially Cu and Pb. These elements presumably form stable organic complexes and chelates in the top organic-rich horizons. A combination of this process together with the great cation exchange capacity of the mosses tissues creates conditions favourable to sorption of trace metals. The capability of metal uptake by mosses was shown to decrease the order $\text{Cu} > \text{Pb} > \text{Zn}$ and Mn (Blagnyte & Paliulis, 2010). This result supports the findings for our study region.

The comparison of the trace metal concentrations in surface soils and the vegetation species showed significant differences for Ni, Mn, and Zn (non-parametric Mann-Whitney U test, $p < 0.05$). Significant differences for Fe and Pb (non-parametric Mann-Whitney U test, $p < 0.05$) were found between the metal contents in the surface soils and lichens, but not the surface soils and mosses. No significant difference for Cu was found between the surface soils and both plant species. All individual vegetation groups of the Lena River Delta region were characterized by lower median concentrations for Cu, Mn, and Zn in comparison with contents for these elements in dry phytomass worldwide, although lichen and moss species had higher median values for Ni and Pb than the data given by Dobrovolsky (2003). Median concentrations for Fe, Cu, Ni, and Zn found in moss species were higher compared to the values reported for mosses of the background areas in northern Eurasia (Evseev, 2003) (Appendix, Tab. VIII).

5.3.2 Element composition of plant species of the Tiksi area

In the Tiksi area, median concentrations of Cu, Mn, and Zn were less in *C. cucullata* in comparison with *Vaccinium vitis-idaea* (Appendix, Tab. VIII), whereas median values of Fe and Pb were higher for lichens than for shrubs. The northern study sites differed significantly from eastern and western study sites by a higher median concentration of Zn in lichens (non-parametric Mann-Whitney U test, $p < 0.05$). The maximum value of Zn was found at the study site TH11 and amounted to 60.5 mg kg^{-1} . The highest contents of Fe, Pb, and Ni were found in lichen species of TH9 in comparison to all other sites. This study site was located in the immediate vicinity to the road leading to Tiksi airport.

Differences in chemical composition for individual vegetation groups (lichens and shrubs) were found depending on the relief forms inhabited (slope, depression) or between the plant species. Considering the western direction area, the lichens of TH3 study site were characterized by

higher concentrations for Fe, Pb, Cu, and Ni when compared to the same species grown in TH4. Mn content in lichens of both sites had the same value. No difference in concentrations for Pb, Cu, and Ni in *Vaccinium vitis-idaea* species inhabited in TH3 and TH5 study sites were found. However, the plants grown in the depressed form of a relief contained higher Fe and Mn than the same species grown in the upper slope. When compared the individual vegetation groups, it was found that all elements were more intensively accumulated by shrubs than by lichens both grown in TH3 study site, except for Pb, the concentration of which has higher in lichens. The study site TH3 was located nearby a winter road. This finding suggests that emissions of fuel combustion from motorized vehicles could be a potential source of these element found in lichen tissues. Additionally, the waste deposit on the eastern exposure of Stolovaya Mountain located north of the study site TH3 could serve as a potential pollution source. In summer 2011, several hypothetic sources of pollutants were observed at the west deposit location area. Combustion products including ash with various kinds of pollutant particles could likely be transferred by dominant winds (south and south-west directions) and precipitated on surrounding territories including the study site TH3. All trace metal contents in surface soils differed significantly from the element contents in lichens (non-parametric Mann-Whitney U test, $p < 0.05$). This finding indicates that soil substrate is not a significant source of trace metals to the lichen species, as it was shown in some studies (e.g. [Chiarenzelli et al, 1997](#)).

Higher concentrations of Fe, Mn, Zn, Cu, and Ni were found in mosses at the study site TH7 in comparison to the site TH4. The topography of the investigated area could be a key factor determining differences in metal distribution for vegetation groups of these two sites. Mosses of TH7 study site were growing on the soil substrate which was developed in the depression and characterized by higher content of the total organic carbon but no significant differences in soil acidity (slightly acid for both sites) when compared to soils of TH4 which were developed on the slope site. Presumably, a part of water-soluble metal forms, being not bound by biogeochemical cycle, was involved to water migration process. Less content of organic carbon and low pH value in soils of TH4 likely contributed to the lateral element migration downslope which, finally, affected the metal uptake by moss species. Median values for Cu, Mn and Zn were smaller, but for Pb and Ni slightly higher in lichen species when compared to the data of [Dobrovolsky \(2003\)](#). Higher median values of Zn were observed in the shrubs in comparison with values of Zn in dry phytomass worldwide ([Dobrovolsky, 2003](#)) (Appendix, Tab. VIII).

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5.3.3 Comparison of vegetation chemical composition in the Lena River Delta and the Tiksi area.

The ash content of plants is an indicator for the intensity of the mineral turnover in plants within an environment. The average ash content of plants worldwide ranges from 3 to 5 %. Herbaceous plants can accumulate double the amount of mineral elements (up to 5 – 7 %) (Opekunova et al, 2002). The majority of tundra plants are characterized by a relatively low so-called actual ash content (amount of elements integrated to plant tissue) of 1.5 – 2 % (Dobrovol'sky, 2003; Moscovchenko, 2006; Protasova, 2008). Results of ash content analysis for different plant species grown in landscapes of the Lena River Delta region and the Tiksi area are shown in Table 10. With 16.4 to 30.0 %, the mosses of the Lena River Delta region showed the highest values of ash content, whereas in mosses of the Tiksi area ash content values ranged from 5.23 % to 8.04 %. Although the median values of the total carbon content in this vegetation group for both investigation sites was similar. This notable variation in ash content in mosses was probably due to a redistribution of aeolian deposits of mineral matter which was transported likely from the surrounding sand banks. According to Dobrovol'sky (2003), a considerable amount of solids in mosses can vary from the total ash content by 40 to 80 %. The median values of ash content in lichens amounted to 6.4 % which was higher than the values found for the lichens of the Tiksi area. The minimum median values for ash content in the lichen species amounted to 1.8 %. As in the deltaic region, shrubs were characterized by similar values for ash content showing a median value of about 3 %. Thus, the differentiation in processes of mineralization is perceptible among the individual vegetation groups which may affect their specific ability of metal uptake.

Table 10: Ash content in vegetation species (in %) grown in the Lena River Delta region and in the Tiksi area.

Study unit	The Lena River Delta			Tiksi area		
	<i>Mosses</i> (<i>n</i> = 12)	<i>Lichens</i> (<i>n</i> = 7)	<i>Bushes</i> (<i>n</i> = 3)	<i>Mosses</i> (<i>n</i> = 2)	<i>Lichens</i> (<i>n</i> = 10)	<i>Bushes</i> (<i>n</i> = 3)
Ash content (in %)	<u>16.4 – 29.9</u> 26.7	<u>5.8 – 8.6</u> 6.4	<u>2.7 – 2.9</u> 2.9	<u>5.23 – 8.04</u> –	<u>0.76 – 15.4</u> 1.71	<u>2.9 – 3.6</u> 3.1

Differences among the individual vegetation groups in terms of element accumulation are evident as various accumulation rates and shown in Figure 40. The relative concentrations for mosses and bushes were reported in terms of ratio to the element concentrations for lichens equal

to 1. Small differences between mosses and lichens were observed in ratios of individual elements (e.g., in Fe ratios). In contrast to mosses, the ratio of Fe, Mn, Ni, and Pb contents in shrubs in the deltaic area and additionally Zn concentrations in the Tiksi area significantly differed from these to vegetation groups. This difference is likely due to morphological organization of these three vegetation groups.

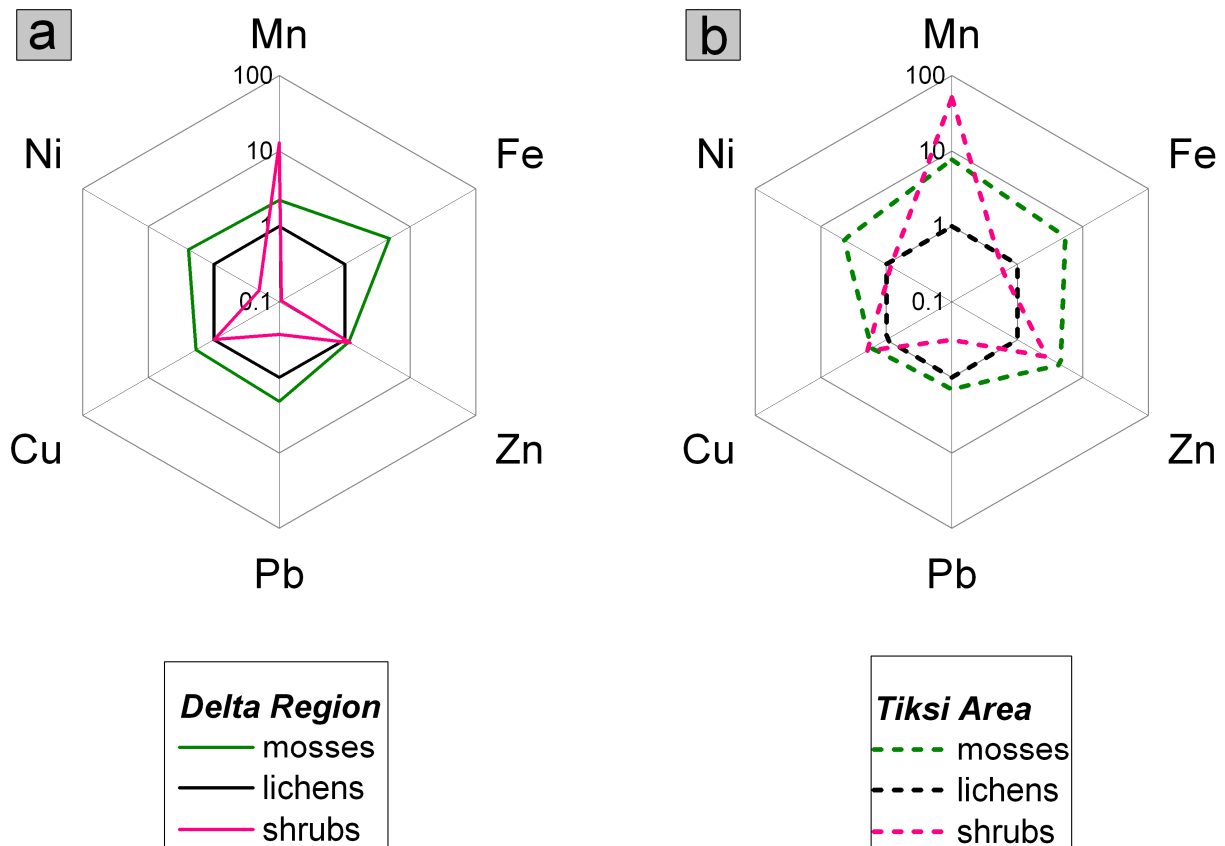


Figure 40: Comparison of element composition of individual vegetation groups inhabited in: (a) – the Lena River Delta region and (b) – the Tiksi area relative to *C. cucullata* (=1).

Calculation of bioaccumulation coefficients (*BC*) for vegetation groups of the Tiksi area and the deltaic region showed consistency in some trace metal accumulation by plants. *Vaccinium vitis-idaea* species were characterized by a high bioaccumulation coefficient suggesting a tendency to accumulate considerable amounts of Mn. This fact was shown in the studies of Ramenskaya (1974), and Chernenkova (2002), confirming that *Vaccinium vitis-idaea* species is a habitual concentrator of Mn. Intensive Mn uptake by this species could possibly be caused by this

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element availability to the plants growing on soils with more acidic environmental reaction. Median concentrations of Fe in the Lena River Delta region mosses species were in a large excess over the maximum concentration in the same species of the area near the town Tiksi. Moss species of the Delta region also tended to accumulate chalcophile elements - Cu and Pb. No consistency to metal accumulation was determined in lichen species for both study regions because of no clear relation of these species with the chemical composition of the soil substrate. Thus, selective metal uptake is governed by the type of the elementary landscape, as well as the plant species. The results of this study are in agreement with the study of [Perel'man \(1975\)](#), who stated at his studies that Fe and Mn significantly contribute to the biogeochemical turnover of tundra landscapes.

All data from all sites of investigated areas (the Lena River Delta and Tiksi area) were used to determine significant differences in trace metal concentrations between vegetation groups applying non-parametric Mann-Whitney U test. Statistical comparison of the Tiksi vegetation data with the data of the Lena River Delta region is shown in Table 11. Significant differences between two areas were found for Cu and Fe ($p < 0.05$) using in the analysis *C. cucullata*. Median values of these elements were higher in the Delta in comparison with the Tiksi area. Significant differences for Cu, Mn, Ni, and Zn between study sites were found using in the analysis *Vaccinium vitis-idaea* species. No significant difference for Mn, Ni, Pb, and Zn was determined between sites using *C. cucullata*, and for Fe and Pb using *Vaccinium vitis-idaea* in the analysis.

A number of publications devoted the attention to vegetation chemical composition of the Arctic region and were used in order to compare the data of this study (Appendix, Tab. IX). Comparison of metal concentrations in mosses for this study showed that concentrations of Mn, Pb, and Zn were in the same range as reported for background area in Norway ([Berg and Steinnes, 1997](#); [Reimann et al, 2001](#)). The range of Pb values in moss species was similar or even less than element concentrations found in *Hylocomium sp.* inhabited in the Faroe Island ([Melnikov et al, 2002](#)), the Pechora River Basin, and Taimyr Peninsula ([Ford et al, 1997](#)). However, the ranges of Pb and Zn concentrations showed higher variation than ranges of the element concentrations in mosses of Canadian Arctic areas ([Wilkie & La Farge, 2011](#)). Median concentrations of Cu and Ni for mosses fallen within the ranges referred for areas on Taimyr Peninsula ([Allen-Gil et al, 2003](#)), Spitsbergen ([Jozwik, 1990](#); [Grodzhinska et al, 1991](#)), and areas

including Nordic countries and a part of Russia (Kola Peninsula) (Äyräs et al, 1997). Although ranges of Cu and Ni concentrations in moss species of the Canadian Arctic had smaller variations than ranges of the element concentrations in mosses of this study. The range of Cu concentrations in mosses inhabited in the Lena River Delta region showed also slightly wider variation in comparison with mosses of the Norwegian background area (Berg and Steinnes, 1997; Reimann et al, 2001).

Table 11: Statistical comparison of the vegetation data of the Tiksi area with similar data obtained from the Lena River Delta region (non-parametric Mann-Whitney U test). The name of the particular region indicated on the table suggests the occurrence of significantly higher element concentrations found for the particular vegetation group.

Element	Highest groups	
	<i>C. cucullata</i>	<i>Vaccinium vitis-idaea</i>
Cu	Delta*	Tiksi*
Fe	Delta*	NS
Mn	NS	Tiksi*
Ni	NS	Tiksi*
Pb	NS	NS
Zn	NS	Tiksi*

* $p < 0.05$

NS, not significant

Pb concentrations in *C. cucullata* of this study were comparable to the values reported for this lichen species from Chukotka Peninsula, Russian Far East (Melnikov et al, 2002), Kola Peninsula, Taimyr Peninsula, and Alaska (Ford et al, 1997). The median concentration of Fe in lichens inhabiting in the Tiksi area lied in the range determined for the same species in Taimyr Peninsula (Allen-Gil et al, 2003). Although Fe content in all vegetation groups of the Lena River Delta were characterized by higher values when compared to all previous studies in Taimyr Peninsula (Allen-Gil et al, 2003), Finland, and Norway (Äyräs et al, 1997).

Vaccinium vitis-idaea species of this study had higher concentrations for Zn and especially, for Mn when compared to the values reported by Ramenskaya (1974) and Opekunova et al (2007) for Kola Peninsula. Median concentrations of Cu and Ni for shrubs fallen within the ranges referred for areas on Taimyr Peninsula (Allen-Gil et al, 2003), Spitsbergen (Jozwik, 1990; Grodzhinska et al, 1991), and areas including Nordic countries and a part of Russia (Kola Peninsula) (Äyräs et al, 1997). Metal concentrations in shrubs were compared with the mean concentrations detected in berries of the same species inhabited in the background area in the

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northern Finland (Pöykiö et al, 2005). For areas of this study, the concentrations of Ni and Pb were low but concentrations of Zn were higher in comparison with concentrations in berries. The difference in the element concentration could likely be explained by features of metal accumulation in various vegetation organs, as well as the properties of soil substrate where these species have been grown.

5.4 Summary

1) The first measurements of trace metal concentrations in permafrost-affected soils of fluvial landscapes of the Lena River Delta and its hinterland in northern Siberia generally showed a high variability in landscape element distribution. It was found that this distribution is presumably caused by differences in the landscape geological structure which reflects therefore, the soil textural composition. Low values of the majority of measured trace metals were found in fine-to-middle grained sand of the northernmost site (second terrace), whereas the sites composed of clayey silt and loam (first and third terraces and the site H-3 of the hinterland) were characterized by higher amounts of most trace elements. Differences in trace metal distribution between the soil suborders showed that the study of chemical composition should be referred primarily to soil genesis which determines the main physical and chemical soil properties.

2) The key feature of studied landscapes in northern Siberia is considerable amounts of Fe and Mn in permafrost-affected soils and peat-forming vegetation. As many studies showed (e.g. Perel'man, 1975; Moskovchenko, 2006; Moskovchenko, 2010), under the humid climatic conditions the elements Fe and Mn are primarily accumulated in tundra landscapes being more sensitive to changes of environmental conditions. The abundance of Fe and Mn contributes significantly to soil chemical composition and likely govern the distribution of trace elements in tundra landscape soils of northern Siberia.

3) It was revealed that micro- and macrorelief features can influence metal distribution in natural permafrost-affected soils. For example, comparison of the polygon rims and polygon centres showed that values of the elements Cu and Pb were higher in polygon centres which were characterized by an accumulation of organic matter and more moist environments. Higher concentrations of some elements (e.g. Fe, Mn, Ni, As, and Zn) were detected in most soil profiles in the deeper minerogenic soil horizons compared to the top soil. This supported a suggestion that the permafrost table, acting as a geochemical barrier, retarded further migration of elements

into deeper horizons. Higher concentrations of most metals were observed in soils of the middle flood-plain compared to the other sites of Samoylov Island. This finding suggested that carbonates and allochthonous material accumulated in alluvial soils during annual inundation are the determining factors controlling sorption of the majority of trace metals at the middle flood-plain.

4) Investigation of biotopes around the settlement Tiksi showed local variations in their soil chemistry for four study units. The eastern sites significantly differed from all other sites by a higher pH suggesting the input of sea-side aerosols and their deposition to the soil surface. No significant variation in metal distribution among studied sites was revealed, except of western sites which were characterised by the highest median values of Ni. Studies of spatial element distribution in geochemically adjacent landscapes of the Tiksi area showed that Fe, Mn, Zn, Cd, and Co migrate more actively than other metals. Most of these elements are leached from gleyic horizons of soils at elevated relief forms and precipitate on oxidizing barriers in soils of slopes and depressions.

5) Soils around the settlement Tiksi differed markedly from the studied soils of the Lena River Delta region by higher values of carbon and nitrogen contents, and enhanced concentrations of the majority of trace elements (As, Cd, Cu, Pb, and Zn) in soils in the presence of more acid reaction in the soil matrix. Element interactions in soils of the Tiksi area were poorly represented than in soils of the Lena River Delta region, in spite of consistent patterns for some elements (e.g. positive correlation As-Fe for both surface and B-horizons, and C-Cu for the surface soil horizons). Differences in acidic soil conditions, lithology, topography, and therefore, features of water migration for the Tiksi area soils in comparison with the deltaic soils likely governed more intensive element migration to adjacent landscapes and their accumulation on acid-base barriers.

6) Chemical composition of individual vegetation groups fully reflects the features of landscape geochemical structure as well as features of biogeochemical element migration in a tundra zone. It is important to note that the intensity of metal accumulation in plants depends not only on the type of a landscape where they grow but also on plant species composition. In this study a combination of these two conditions regulating plant chemistry was shown on the example of three vegetation groups – mosses, lichens, and shrubs, all widely spreading in the landscapes of two investigated geomorphological units. The mosses and lichen species inhabited in the deltaic

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region accumulated Fe and Cu more actively than these species in the Tiksi area whereas the shrubs of the Tiksi area were apt to accumulate Cu, Mn, Ni, and Zn when compared to the Lena River Delta region. A considerably high amount of Mn was accumulated by *Vaccinium vitis-idaea* species in comparison to other individual vegetation groups. This finding reflects strong relation with soil chemical composition as well as their biogeochemical specificity which coincides with the studies in other northern areas.

7) In a regional scale the studied area in northern Siberia including the Lena River Delta and its hinterland is pristine and can serve as a reference region for determining human influences on permafrost-affected landscapes or comparing similar pristine areas in the Arctic region. However, an early indicator of local human impact was determined at one studied site on Samoylov Island. The area Tiksi was also considered as pristine except for some individual sites, where there were signs of a local impact. The enrichment of Pb and Zn in the surface horizons and vegetation samples of selected study sites around the town Tiksi can indicate local pollution related to fuel emission (for Pb) and mining operations north of the town (for Zn). However, lack of the data makes this conclusion difficult to sustain and the existing dataset needs to be expanded.

5.5 Laboratory experiment. Trace element distribution in soils caused by freezing.

In further description of the experiment results, the terms “unfrozen soil columns (UFC)” and “frozen soil columns (FC)” refer to the columns from the experimental BOX 1 and BOX 2, respectively.

5.5.1 Temperature regime and water distribution in soil columns

The soil temperatures of the unfrozen columns were positive during the whole period of the experiment (Fig. 41a) and averaged 20.0 ± 2.3 °C. In spite of the temperature variation during the experiment, the average temperature difference within the soil column depth was negligible and varied from 0.01 °C between 6 cm and 4 cm to 0.05 °C between 4 cm and 2 cm of the soil column depth. The period of a freezing experiment was accomplished in three stages: (I) constantly and relatively slow decreasing of the soil temperature from bottom upwards, (II)

continuously but relatively fast decreasing of the soil temperature, and (III) fluctuating soil temperature within the freezing columns (Fig. 41b). During stage I, a temperature gradient was propagated upward through the columns and varied from 0.14 °C/mm to 0.19 °C/mm between 6 cm and 2 cm depth of the soil column. The average soil temperature in the lower part of the columns was negative during the whole experiment. The average soil temperatures in soil layers between 2 and 6 cm depths varied from -0.79 ± 0.33 °C in the lower part to 5.87 ± 0.40 °C in the upper part of the column, respectively. During stage II, the average soil temperatures dropped down being approximately from 4 °C to 2 °C less in soil layers between 2 cm and 6 cm of a column depth, respectively. The temperature gradient varied from 0.07 °C/mm to 0.17 °C/mm being propagated upward between 2 and 6 cm of a soil column depth. The average freezing rate accounted for approximately 0.6 mm/h. The minimum soil temperatures at the measured depths were observed between 139 and 157 h after starting the experiment (shaded area). In stage III, the soil temperature regime was characterized by instability because of technical reasons. The average temperatures varied from 2.78 ± 1.24 °C at 2 cm to -1.78 ± 0.52 °C at 6 cm of the soil column depth. The final vertical distribution of gravimetric water content in unfrozen and frozen soil columns is shown in Figure 42. After the experiment, no evident changes in soil structure (homogeneity, colour) in soil columns without freezing were observed. In the absence of the vertical temperature gradient, no redistribution of gravimetric water content within these soil columns was found (Fig. 42a). In the frozen columns, the freezing front at the end of the experiment was detected at 4.3 ± 0.2 cm depth. In frozen soil layers between 6 and 8 cm depth, small ice crystals were observed. The gravimetric water content changed during the experiment: the maximum median gravimetric water content ($n = 4$; because of a technical problem, only four soil columns affected by freezing were used for laboratory analyses) was observed in the bottom part of the columns at depth of 5 – 6 cm and amounted to 24.5 ± 2.1 % (Fig. 42b). In the top soil layers, the gravimetric water content decreased downwards and varied from 5.9 % to 4.8 % within the upper 0 – 3 cm contaminated soil layers of columns affected by freezing. These values account for 48.3 and 63.3 % of water loss (in comparison with the initial gravimetric water content), respectively.

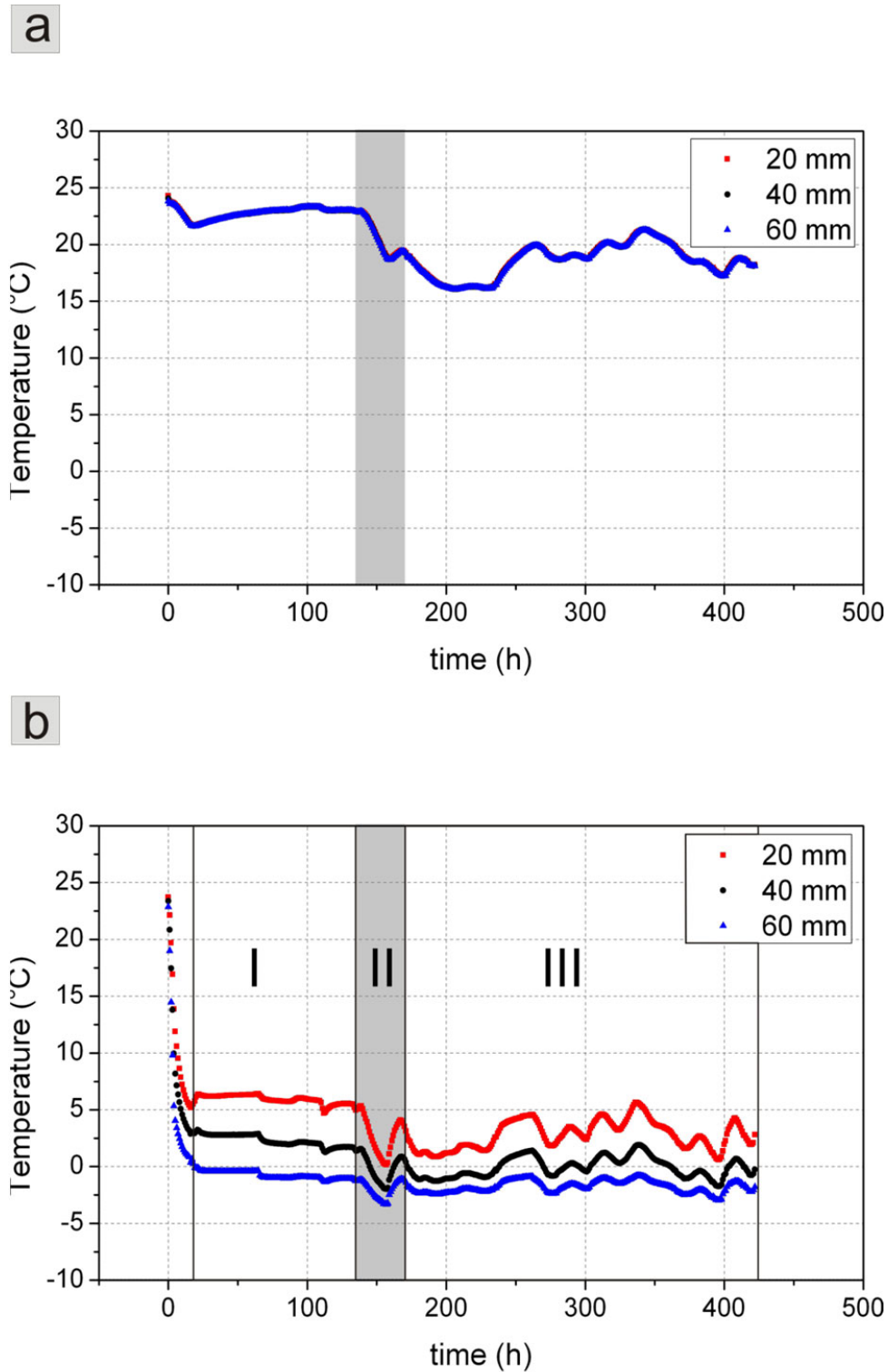


Figure 41: Soil temperature at column depths 2, 4, and 6 cm: (a) – in unfrozen soil columns (UFC) and (b) – in frozen columns (FC). Three stages of the freezing process are denoted by roman numerals.

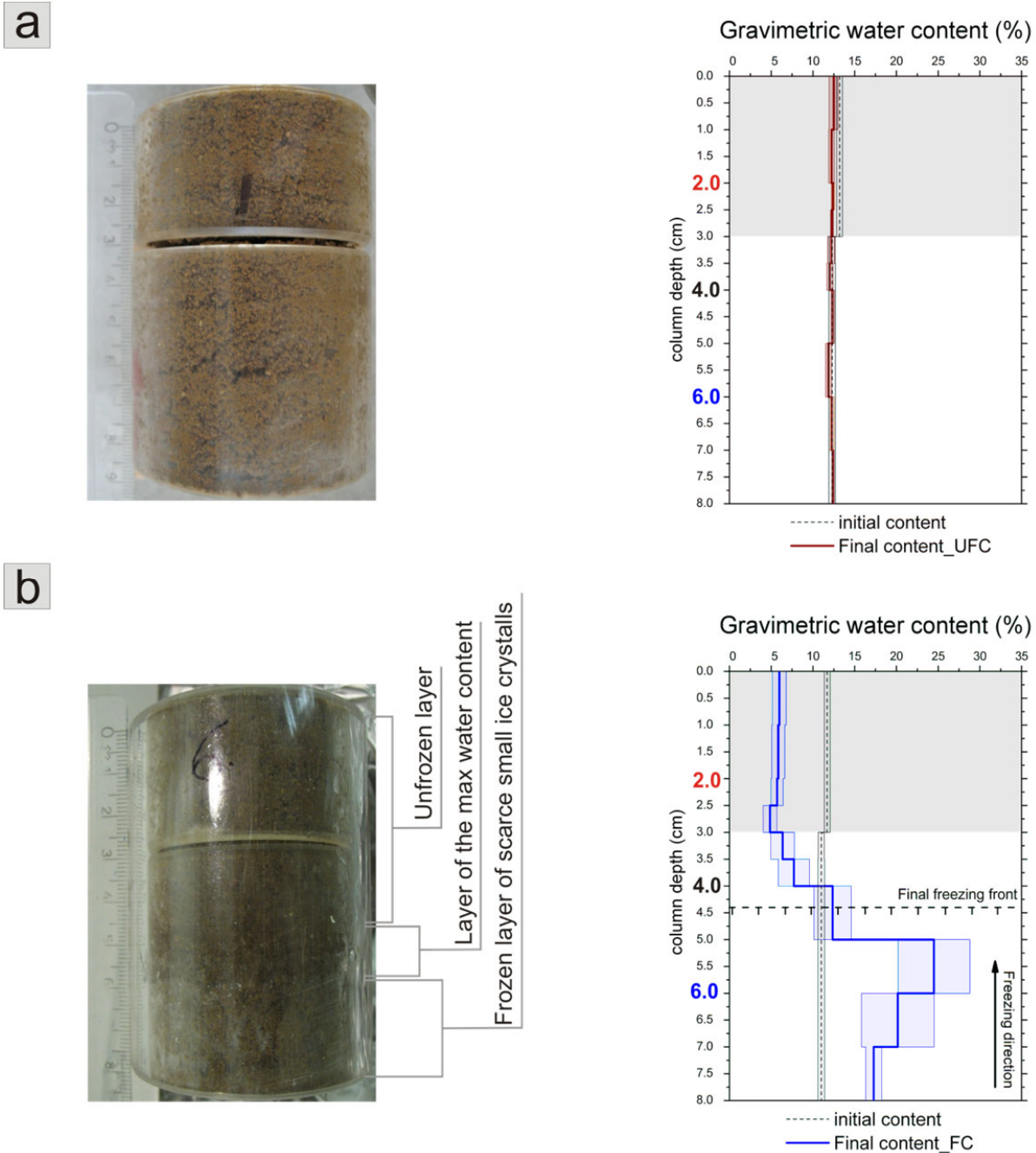


Figure 42: Water content distribution after the experiment in soil columns: (a) – without freezing (UFC) and (b) – affected by freezing from bottom upward (FC). The solid line indicates the mean gravimetric water content and the hatched area denotes the standard deviation (SD) of soil column replicates ($n = 5$ for UFC; $n = 4$ for FC). Shaded area indicates a column part filled by contaminated soil material. The horizontal dashed dark blue line denotes the final average freezing front for frozen columns. Red-, black-, and blue-marked values indicate the depth of temperature sensors installation in control columns.

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5.5.2 Vertical redistribution of Cd and Pb within the columns

5.5.2.1 Cd redistribution

The experimental results of the vertical redistribution of Cd and Pb within the soil columns are summarized in Figure 43. After the experimental run, the final element distributions within the unfrozen and frozen soil columns differed from the initial one. The final concentrations of Cd in the top (initially contaminated) column part had decreased and varied from $38.2 \pm 2.0 \text{ mg kg}^{-1}$ to $28.6 \pm 0.5 \text{ mg kg}^{-1}$. These results accounted for approximately 70 and 54 % of the initial Cd content, respectively. In the lower (uncontaminated) column part, concentrations of Cd increased between $24.6 \pm 0.9 \text{ mg kg}^{-1}$ and $4.7 \pm 0.9 \text{ mg kg}^{-1}$ which are 415 and 72 times higher the initial Cd concentration of the uncontaminated soil layer, respectively.

The variation of Cd concentrations was observed in soil layers between 0 – 4 cm depths of all frozen columns. The highest Cd concentrations were found in the top soil layers, they amounted to $65.5 \pm 7.8 \text{ mg kg}^{-1}$ which was about 25 % higher than the initial element concentration and almost two times more than the final Cd content in the top soil layers of columns without freezing. Cd concentrations were about 30 % less in soil layers between 1 – 2 cm and 20 % less in soil layers between 2.5 – 3 cm soil column depths than in unfrozen columns at the same depths. It should be noted that Cd penetrated deeper into the uncontaminated soil column part of the unfrozen columns compared to the frozen soil columns. In soil layers between 3 and 8 cm depth of frozen soil columns, Cd content decreased downwards varying from $17.3 \pm 0.8 \text{ mg kg}^{-1}$ to $0.08 \pm 0.04 \text{ mg kg}^{-1}$. The deviation of Cd concentrations between the frozen and unfrozen columns varied from 14 % in the top of the initially uncontaminated column part to 0.1 % in the bottom of the columns. This finding suggests less extended penetration of Cd downwards within the frozen soil columns in comparison with the unfrozen soil columns. The final Cd concentrations significantly differed between soil layers of the soil columns without freezing and the soil columns affected by unidirectional freezing at the column depths between 0 and 4 cm and between 5 and 6 cm, respectively (non-parametric Mann-Whitney U test, $p < 0.05$).

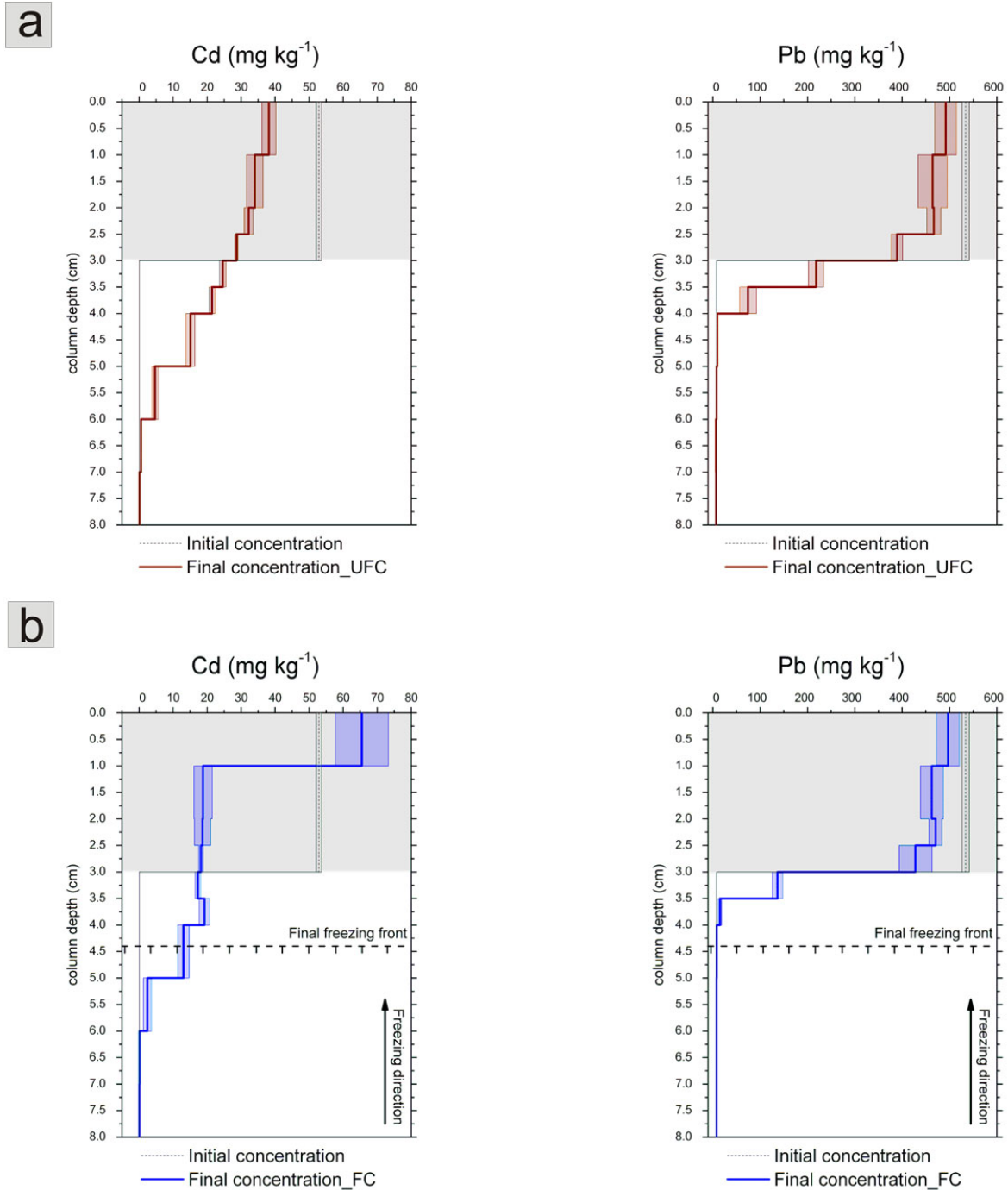


Figure 43: Redistribution of cadmium and lead after the experiment in soil columns: (a) – without freezing effect (UFC) and (b) – affected by freezing from bottom upward (FC). The solid line indicates the mean gravimetric water content and the hatched area denotes the standard deviation (SD) of the soil column replicates. Shaded area indicates a column part filled by contaminated soil material. The horizontal dashed dark blue line denotes the final average freezing front for frozen columns

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5.5.2.2 Pb redistribution

The final concentrations of Pb in soil layers of columns without freezing decreased to a lesser degree than the final Cd concentrations. Within the upper soil column parts of 0 – 3 cm depth, Pb concentrations varied from $492 \pm 22.7 \text{ mg kg}^{-1}$ at the top of the soil columns to $389 \pm 12.0 \text{ mg kg}^{-1}$ in the layer nearest to the initially uncontaminated soil column part, which accounted for 92 % and 74 % from the initial Pb content, respectively. Initially uncontaminated soil layers contained from $218 \pm 16.0 \text{ mg kg}^{-1}$ to $7.1 \pm 0.3 \text{ mg kg}^{-1}$ Pb decreasing downwards. The first concentration approximately 27 times exceeded the initial Pb concentration of the lower soil column part.

Pb distribution within the upper part of frozen soil columns (FC) was similar to the element distribution in the control unfrozen soil columns (UFC). In the upper, (contaminated) soil column part, the concentration of Pb decreased with depth from $497 \pm 24.2 \text{ mg kg}^{-1}$ to $428 \pm 34.8 \text{ mg kg}^{-1}$ which accounted for 93 % and 81 % of the initial element concentration, respectively. Similar to Cd, Pb penetration to the uncontaminated part of soil columns affected by freezing was less expanded than within control soil columns. The concentrations of Pb at 3.5 – 4 cm column depth were about 13 % less than in the unfrozen columns. A significant difference in the final Pb distribution was found between the freezing columns and the columns without freezing effect only for soil layers at 3 – 3.5 cm and 3.5 – 4 cm column depths (non-parametric Mann-Whitney U test, $p < 0.05$).

5.5.2.3 Relative element concentration decrease and available metal fractions in soil columns

Relative element concentration decrease (ϵ) of Cd and Pb were calculated for soil layers of the initially contaminated soil column part of 0 – 3 cm depth and expressed in % (Tab. 12). These results showed that in initially contaminated layers of all experimental soil columns, median values of Cd were higher than values of Pb. This finding was shown to decrease of Cd concentrations in the initially contaminated soil layers to a greater extent in comparison with Pb concentrations. No remarkable difference between relative concentrations of Pb for soil layers of unfrozen and frozen columns was observed. In soil layers of columns without freezing, Pb median relative concentrations varied from 9 to 27 %, and in soil layers of columns affected by freezing, these values ranged from 7 to 19 %, in both cases increasing with the column depth. Relative concentrations of Cd in soil layers of frozen columns were half the values for Cd

observed in soil layers of unfrozen columns. A concentration decrease of this metal varied from 65 to 66 % in 1 – 3 cm soil layers of columns affected by freezing, whereas relative concentrations ranged from 29 to 46 % in soil layers of columns without freezing at the same column depth. The negative value of Cd relative concentration indicated an increase of this element concentration in the top of the soil columns affected by freezing in comparison with the initial values.

Table 12: Mean values of relative metal concentration decrease (ϵ) calculated for Cd and Pb in soil layers of initially contaminated column parts of 0 – 3 cm thickness, where UFC – soil columns without freezing and FC – soil columns affected by unidirectional freezing.

Contaminated layer (cm)	Relative element concentration decrease (%)			
	ϵ_{Cd}		ϵ_{Pb}	
	UFC	FC	UFC	FC
0.0 – 1.0	28	-24	8.0	7.0
1.0 – 2.0	36	64	13	13
2.0 – 2.5	39	65	13	12
2.5 – 3.0	46	66	27	20

The vertical distribution of mean available fractions of Cd and Pb (r_c) in the soil columns is shown in Figure 44. Additionally, a conceptual scheme of temperature conditions during the experiment is shown in Figure 44b for frozen soil columns. From both column experiments, it was found that the relative content of mobile forms of Cd is higher than relative concentrations of Pb. These results show also that Cd possessed a higher ability to penetrate downward through the soil matrix than Pb. In soil columns without the temperature gradient, a gradual decrease of mobile forms of Cd and Pb was observed starting from 3 – 4 cm column depth whereas only small variation of relative concentrations of these elements were observed in soil layers at 0 – 3 cm column depth. Comparing these results with the results of the water content redistribution within the soil columns without freezing, no similarities between the redistribution of potentially mobile metal forms and water content was found. This finding suggests that element migration must have occurred independently from water content distribution. Concentrations of available fraction of Cd and Pb were slightly higher in the upper soil layers of columns that have undergone unidirectional freezing. The concentrations of these elements in the experimental columns affected by freezing (FC) did not change in the same way as in soil columns without temperature gradient (UFC). A higher variation of available fraction content of potentially mobile forms of Cd was evident in the transition zone of 0 – 4 cm depth of frozen soil columns.

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In the zone of the frozen soil layers from 6 cm to 8 cm depth, the concentrations of Cd went down in comparison with results of unfrozen soil columns. The concentrations of available form of Pb also rapidly decreased in soil layers deeper than 3 cm when compared with unfrozen soil columns. Comparing both graphs, it is evident that the freezing affected the vertical metal distribution.

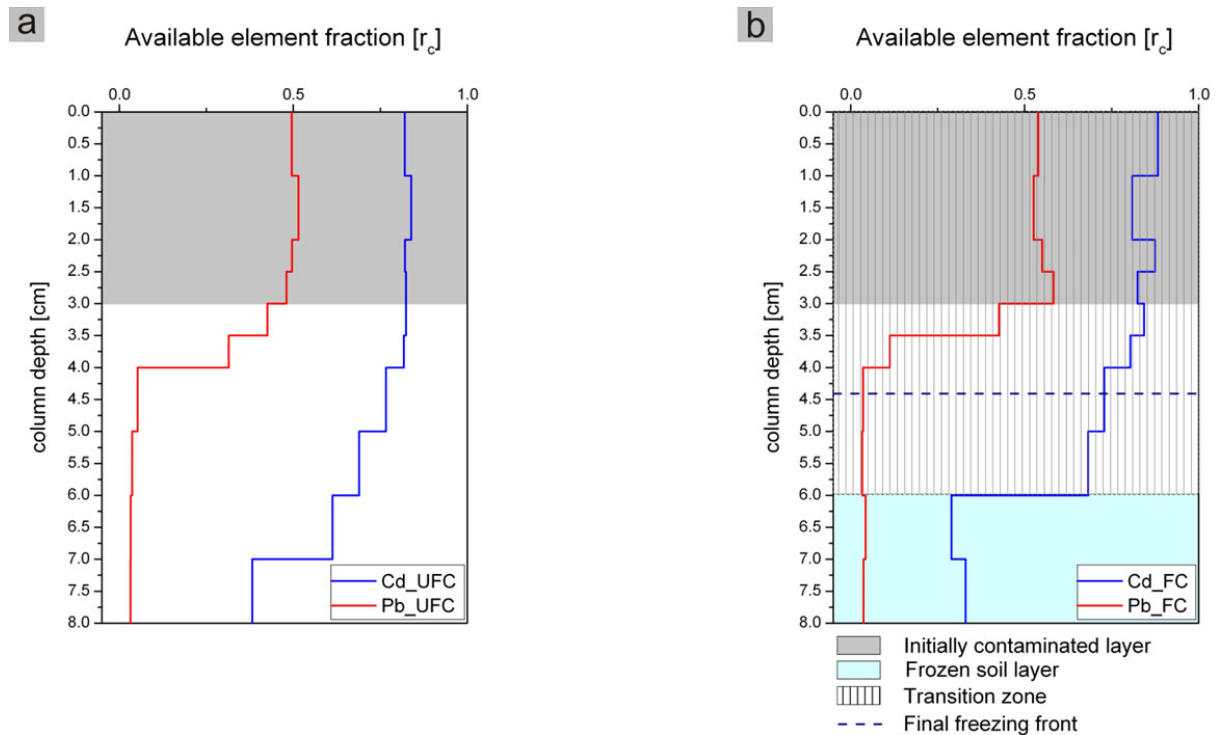


Figure 44: A conceptual graph showing Cd and Pb available fraction distribution versus soil column depth in: (a) – unfrozen soil columns (UFC) and (b) – soil columns (FC) affected by unidirectional freezing. The grey shaded area indicates the initially contaminated column part. The light blue shaded area indicates a soil layers with temperatures below zero during the experiment. The vertical line shaded area represents a transitional zone where temperature variation took place during the experiment. The dark blue dashed line indicates the approximate level of the final freezing front.

Based on the experimental results, it was found that the moisture transfer process played a minor role in the vertical redistribution of metal ions in unfrozen soil columns. In the unfrozen soil columns, a notable migration of Cd and Pb into the uncontaminated column part occurred regardless of negligible changes in water content within the whole soil column depths. In the

experiments, the soil material was characterized by a coarse-grained texture and unsaturated conditions possessing a relatively low capillary conductivity. It suggests that a state of balance between soil matrix potential and gravitational potential energy gradient took place, which did not permit a notable movement of water in unfrozen soil columns. Therefore, it can be concluded that metal ions could move independently through water films along their concentration gradient and partly under the influence of the gravitational force. The obtained results supported the experimental studies of [Cary & Mayland \(1972\)](#) where they examined the movement of salt ions in the unsaturated soil system.

The experiment showed that the penetration of Cd into deeper soil layers was more intensive in comparison with Pb penetration in all investigated soil columns. Because the soil comprised a low amount of organic carbon, the organic matter can be neglected as a factor governing the adsorption of Pb in the soil columns. A decreased mobility of Pb can be explained by occurrence of a high amount of Fe in the soil matrix. According to [Ainsworth et al \(1994\)](#), more than 90 % of Pb and only about 10 % of Cd are adsorbed by Fe hydroxides in a mineral soil matrix. Because of the individual chemical element properties, [Vodyanitsky et al \(2012\)](#) and [Vodyanitsky \(2013\)](#) considered Pb to be a less hazardous element in soils in comparison with more mobile metal ions (e.g. Cd). Therefore, it is necessary to note that sorption characteristics of a soil system together with individual chemical properties of potentially hazardous elements should be considered as an important mechanism which affects the ion transport in soils when estimating a risk of metal pollution.

This experiment showed that the temperature gradient in frozen soil columns (FC) contributed to the Cd migration in addition to the concentration diffusion process along the concentration gradient in the soil columns. The Cd distribution in the frozen soil columns at the end of the experiment run may be described in the following way. On the one hand, a further penetration of Cd to deeper soil layers was restricted by a low permeability of the frozen soil layer. On the other hand, freezing process resulted in a relatively higher mobility of Cd in the upper part of the soil columns and expulsion of this mobile element upward. At the beginning of the experiment, the water contained in the bigger, uncontaminated part of the soil columns started to migrate towards the freezing front the upward movement of which was accompanied by initiation of the ice crystal formations as it was described in Subsection 2.2.3.

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It can be assumed that during stage I of the experiment, the freezing front was still in the zone of the uncontaminated soil layers, and therefore, portions of water moving toward the freezing front came mainly from the uncontaminated parts of columns. At the same time, independent diffusion of metal ions along the chemical gradient could occur until the frozen soil layer, where its permeability was at the minimum level and delayed further ion migration. Several permafrost studies considered a frozen zone as a geochemical barrier (e.g. [Ostroumov et al, 1998](#); [MacGregor, 2000](#); [Alekseev et al, 2003](#)). However, the studies of [Makarov \(1988\)](#) and experiments of [Ershov et al \(1995\)](#) showed that ion migration of some elements occurs even in frozen soils. The dataset obtained from this experiment could neither support nor confute the findings of the previous studies.

During stage II, the increase of the temperature gradient resulted in a further propagation of the freezing front upwards and therefore, further water migration towards the frozen area and the formation of new ice crystals. Two conjoined processes could occur during the ice crystal formation which could influence Cd migration: (1) frost heaving and (2) ion expulsion towards the unfrozen soil layers. The first process can be neglected in coarse-grained soil system: firstly, because bigger soil particle pore space in comparison with fine-grained soils may permit a further propagation of the freezing front. Secondly, the presence of soluble ions in water contained in the interporous space may lead to the following: during freezing of water which comprises soluble chemical compounds, the formed ice tries to exclude these compounds from its structure, therefore increasing the concentration of elements in the zone of unfrozen soils. Increased concentrations of water solutions may decrease the freezing point of water. Therefore, the unfrozen water can continue to migrate to the freezing front and in doing so, decrease the effect from frost heaving ([Cary & Mayland, 1972](#); [Cary et al, 1979](#); [Chamberlain, 1983](#); [Henry, 1988](#)). The ion expulsion in freezing soils results from the decrease of water film thickness and therefore, the pressure of the water film adsorbed by soil particles. At the same time, the pressure decrease may enhance so-called disjoining force between soil particles ([Padday, 1970](#); [Henry, 1988](#)). This mechanism of ion redistribution was observed in studies of [Hallet \(1978\)](#), [Chuvilin et al \(1998\)](#), [Chuvilin \(1999\)](#), and [Ostroumov et al \(2001\)](#) and described in experiments of [Baker et al \(1990\)](#), [Gay & Azouni \(2003\)](#), and [Bing & He \(2011\)](#). The degree of ion expulsion depends on the rate of freezing as well as on the soil material properties ([Anisimova, 1973](#)). The studies mentioned above showed that the ion expulsion effect occurs mainly in coarse-grained soil

material, whereas in fine-grained soils high concentration of water soluble ions is observed right above the freezing front.

In this experiment, no significant ion redistribution has occurred in the upper part of the frozen columns during the stage III. The major part of water seemed to have migrated downwards and accumulated in the initially uncontaminated soil column parts. At the same time, in the initially contaminated soil column parts, the thickness of water films adsorbed by soil particles became smaller and therefore, could not serve as a media for the metal ion transport. Therefore, it was concluded that the ion redistribution occurred mainly during stages I and II of the experiment.

5.6 Summary

This experiment, performed with coarse-grained sand, showed that a number of transport mechanisms were involved in the soluble ion form migration in the soil system. At this stage of the study, the following conclusions can be drawn:

1. In the frozen soil columns, no clear relation between water migration and the metal distribution was found. Diffusion along the concentration gradient was shown to be the most important mechanism controlling the migration of water soluble forms of Cd and Pb.
2. Physical and chemical soil properties (e.g. soil texture, sorption ability properties) and differences of element characteristics of Cd and Pb (e.g. ionic charge, ionic radius) might be essential in controlling the mobility of these metals and therefore, played an important role in governing the metal redistribution in the soil columns.
3. An accumulation of Cd in the upper soil layers was observed as a result of the expulsion of soluble Cd ions from the frozen soil interface.
4. A decrease of the Cd mobility in the lower parts of the frozen columns in comparison with the unfrozen columns, suggests that frozen soils acted as a temporal geochemical barrier restricting a further diffusive transfer of Cd downwards. However, more experiments are required to confirm these results of the experiment.
5. The obtained experimental data is still not enough to understand all mechanisms of mentioned processes that occur under the natural environments. To gain a better understanding of these mechanisms, further investigations are needed to provide quantitative explanations. Future

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studies should focus on the processes of ice lens formation and this effect on the behaviour of different contaminant substances. The interactions between contaminant solutes and freezing processes in soils should be considered, since the presence of soluble ions in freezing water may strongly affect the chemical potential of water and, by decreasing its freezing point, control the process of ice lens formation in soils.

6. Conclusions and Outlook

The presented study contributes to the knowledge of the concentrations and the distribution of trace metals in permafrost-affected environments of the Siberian Arctic. The key findings are:

- The landscape element distribution in soils of northern Siberia is characterized by a high variability being related to the factors such as lithology and relief characteristics, soil texture, organic carbon content, soil acidity, and temperature and water regimes. The variability of such elements as Cu and Cd is mainly controlled by the soil organic carbon content, whereas a variability of Zn and Pb depends on the occurrence of fine-grained material of the studied soils. In most studied soil profiles, the abundance of Fe and Mn oxides and hydroxides governed the distribution of As and Ni. All factors mentioned above contribute to a high diversity of permafrost-affected soils as well as to a homeostasis of the natural tundra landscapes.
- Permafrost conditions and cryoturbation processes play a particular important role in the metal distribution in the soil matrix by forming geochemical barriers which impede element migration. Enhanced concentrations of Fe, Mn, Ni, As, and Zn were observed right above the permafrost table in polygon structured soils.
- Soils around the settlement of Tiksi were characterized by enhanced concentrations of the majority of trace elements (As, Cd, Cu, Pb, and Zn) compared to soils of the Lena River Delta. Element correlations in soils of the Tiksi area were, however, poorer represented than in soils of the Lena River Delta region. These differences are presumably caused by various composition of underlying deposits (clay shale), roughness of the landscape, acidic soil conditions, which resulted in potentially higher element mobility in soils of the Tiksi area.
- The concentrations of the majority of metals in these studied environmental components (soils and plants) were similar to those reported for other northern regions. Therefore, obtained results can serve as a reference point to compare to other areas in the Arctic and to carry out a geocological monitoring.

The knowledge about the background levels of trace metals is important not only for an assessment of potential long-range anthropogenic effects on the investigated area but also for understanding the processes of biogeochemical turnover rates controlled by climatic factors. In order to gain more information about the regional geochemical characteristics of the studied area,

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investigations on chemical composition of biotic and abiotic environmental components (e.g. rocks, sediments, surface and groundwater, and vegetation) should be carried out to a greater extent. A larger grid-like database, relying on the topography of the area, could then provide the basis for upscaling the results on a regional level with the application of geographical information system (GIS) analyses.

Further investigations should focus on the processes of deposition, accumulation, leaching, translocation, and transformation of trace metals in permafrost-affected soils and need to be studied in greater detail in order to estimate possible risks from both climate change and anthropogenic pollution on the Arctic ecosystems. Because the soils of the northern Siberia region are characterized by occurrence of a huge amount of organic matter, future studies should address the role of soil organic matter (e.g. fulvic and humic acids), which contributes significantly to metal redistribution in permafrost-affected environments. To deepen the understanding of the role of permafrost as a geochemical barrier for various chemical elements, chemical characteristics of soils below the permafrost table together with factors affecting the seasonal variability of elements (upward and downward migration) should be studied as well.

In order to understand the processes of contaminant migration in cold environments, a laboratory experiment was carried out. Comparing the results with the available literature, it was concluded that diffusion remains the major mechanism which controls vertical metal distribution in an unsaturated soil system. This study demonstrated that the effect of unidirectional freezing caused the expulsion of mobile Cd towards the unfrozen soil column part, whereas no similar effect of Pb redistribution was observed. This finding suggests that the element characteristics and their interactions with the soil matrix are one of the most important factors controlling the metal migration in freezing soils. A delay of the vertical distribution of Cd in frozen soil columns was explained by the decreasing permeability of frozen soil layers for metal ions.

The following practical aspects should be considered and implemented in future experiments:

- a) The temperature conditions should be stabilized to get a clear effect of freezing on the contaminant redistribution.
- b) Different soil material types (e.g. clay, fine-grained silt, fine-grained sand, coarse sand) with various characteristics (e.g. low/high organic carbon, low/high cation exchange capacity, saturated and unsaturated conditions) as well as various metal concentrations

(low/high) should be used in the experiments to estimate the effect of freezing on the soil sorption capacity as well as to understand how the presence of contaminant solutes influences the processes of ice lens formation and frost heave.

- c) Future studies should include several freeze-thaw cycles in order to simulate annual thawing and freezing processes which occur in natural environments and may affect the redistribution of water soluble elements in soils. Furthermore, future experiments should focus on effects of metal redistribution caused by propagation of freezing from the top and bottom of soil columns.

The experimental studies have important implications for the fate and transport of contaminants in permafrost-affected environments. It is particularly important for estimating the ecosystem strengths in response to potential increase of human impact as well as to global warming in Polar Regions. The mechanisms which influence the redistribution of water soluble elements need to be studied to a larger extend. Furthermore, these processes, which occur in permafrost-affected environments, should be introduced into the existing models of contaminant transport in soils as well as to supplement the existing models of water, solute and heat transport.

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Appendix

Table I: General field information of investigation sites of the Lena River Delta and its nearby hinterland.

Sites ID	Sampling location	Landscapes description
3rd terrace		
3T-1	72°48'31.31" N 124° 54' 43.89" E	Sedge/moss tundra Dominant species: <i>Carex aquatilis</i> , <i>Poa arctica</i> , <i>Eriophorum medium</i> , <i>Salix sp.</i> , <i>Luzula sp.</i> , <i>Saussurea sp.</i>
3T-2	72°34'24.04" N 127° 14' 14.73" E	Typical polygonal sedge/moss tundra Dominant species: <i>Carex sp.</i> , <i>Poaceae sp.</i> , <i>Dryas punctata</i> , <i>Hylocomium sp.</i>
2nd terrace		
2T-1	73°10'26.29" N 124° 34' 29.80" E	Typical moss/lichen tundra Dominant species: <i>Carex sp.</i> , <i>Cassiope tetragona</i> , <i>Luzula sp.</i> , <i>Cladonia sp.</i> , <i>Thamnia vermicularis</i> , <i>Hylocomium sp.</i>
1st terrace		
1T-1	71°59'11.55" N 127° 02' 35.29" E	Forest herbs/lichen/moss tundra Dominant species: <i>Ledum palustre</i> , <i>Betula nana</i> , <i>Carex sp.</i> , <i>Eriophorum medium.</i> , <i>Luzula sp.</i> , <i>Pedicularis sp.</i> , <i>Hylocomium sp.</i> , <i>Aulacomnium sp.</i>
1T-Rim1	72°22'17.66" N 126° 29' 11.66" E	Elevated herbs/lichen/moss tundra, polygon rim Dominant species: <i>Dryas octopetala</i> , <i>Salix glauca</i> , <i>Stereocaulon alpinum</i> , <i>Thamnia vermicularis</i> , <i>Dactylina arctica</i> , <i>Hylocomium sp.</i> , <i>Aulacomnium sp.</i>
1T-Ce1	72°22'17.66" N 126° 29' 11.66" E	Sedge/moss tundra, polygon centre Dominant species: <i>Carex aquatilis</i> , <i>Eriophorum medium</i> , <i>Hylocomium sp.</i>
1T-d	72°22'25.60" N 126° 29' 44.30" E	Sedge/moss polygon tundra Dominant species: <i>Carex sp.</i> , <i>Eriophorum sp.</i> , <i>Hylocomium sp.</i>
High floodplain		
HF-Rim2	72°22'19.46" N 126° 28' 42.74" E	Herbs/moss tundra, poorly defined polygon rim Dominant species: <i>Salix sp.</i> , <i>Arctagrostis arctostaphulos</i> , <i>Aulacomnium sp.</i>
HF-Ce2	72°22'19.55" N 126° 28' 41.77" E	Sedge/moss tundra, polygon centre Dominant species: <i>Carex sp.</i> , <i>Arctagrostis arctostaphulos</i> , <i>Aulacomnium sp.</i>
Middle floodplain		
MF-1	72°22'51.61" N 126° 28' 28.37" E	Shrub/sedge cover Dominant species: <i>Dischampsia Caespitosa</i> , <i>Arctophila fulva</i> , <i>Salix sp.</i>
Hinterland		
H-1	71°10'26.29" N 124° 34' 29.80" E	Slope of Chekanovsky Ridge, herbs/moss southern tundra Dominant species: <i>Betula nana</i> , <i>Ledum palustre</i> , <i>Cassiope tetragona</i> , <i>Vaccinium vitis-idaea</i> , <i>Polygonum viviparum</i> , <i>Hylocomium sp.</i>
H-2	70°55'22.76" N 125° 33' 3.13" E	Slope of Chekanovsky Ridge, shrub/moss forest tundra Dominant species: <i>Betula nana</i> , <i>Ledum palustre</i> , <i>Eriophorum medium</i>
H-3	69°23'56.83" N 123° 49' 33.96" E	Slope of Chekanovsky Ridge, Larix/shrub/moss northern taiga Dominant species: <i>Larix Sibirica</i> , <i>Betula nana</i> , <i>Alnus crispa</i> , <i>Salix sp.</i> , <i>Empetrum nigrum</i> , <i>Ledum palustre</i> , <i>Hylocomium sp.</i>

Appendix

Table II: General field information of investigation sites of an area around the settlement Tiksi.

Sites ID	Sampling location	Landscape description
TH1	71° 33' 57.2" N 128° 50' 45.5" E	Typical herb/lichen-moss tundra Dominant species: <i>Salix sp.</i> , <i>Betula nana</i> , <i>Eriophorum sp.</i> , <i>Carex sp.</i> , <i>Polygonum viviparum</i> , <i>Puroloa rotundifolia</i> , <i>Saxifraga punctata</i> , <i>Pedicularis sp.</i> , <i>Dactilina arctica</i> , <i>Thamnolia vermicularis</i> , <i>Peltigera aphthosa</i> , <i>Aulacomnium sp.</i>
TH2	71° 33' 55.8" N 128° 50' 42.0" E	Typical herbs/moss-lichen tundra Dominant species: <i>Ledum palustre</i> , <i>Cassiope tetragona</i> , <i>Polygonum sp.</i> , <i>Vaccinium vitis-idaea</i> , <i>Vaccinium uliginosum</i> , <i>Cetraria cucullata</i> , <i>Alectoria sp.</i> , <i>Aulacomnium sp.</i>
TH3	71° 37' 05.4" N 128° 46' 29.0" E	Typical shrubs/ herbs/moss-lichen tundra Dominant species: <i>Salix sp.</i> , <i>Betula nana</i> , <i>Carex sp.</i> , <i>Cassiope tetragona</i> , <i>Pedicularis capitata</i> , <i>Dryas punctata</i> , <i>Polygonum sp.</i> , <i>Vaccinium vitis-idaea</i> , <i>Eriophorum sp.</i> , <i>Saxifraga sp.</i> , <i>Alectoria ochroleuca</i> , <i>Cetraria cucullata</i> , <i>Aulacomnium sp.</i>
TH4	71° 37' 17.3" N 128° 49' 43.9" E	Typical herbs/ lichen-moss tundra Dominant species: <i>Carex sp.</i> , <i>Salix sp.</i> , <i>Pedicularis sp.</i> , <i>Pedicularis capitata</i> , <i>Dryas punctata</i> , <i>Merckia physodes</i> , <i>Dactylina arctica</i> , <i>Cladonia sp.</i> , <i>Alectoria sp.</i> , <i>Cetraria cucullata</i> , <i>Aulacomnium sp.</i> , <i>Hylocomium sp.</i>
TH5	71° 37' 26.1" N 128° 48' 21.9" E	Typical sedge/ moss tundra Dominant species: <i>Carex sp.</i> , <i>Salix sp.</i> , <i>Betula nana</i> , <i>Polygonum sp.</i> , <i>Polemonium coeruleum</i> , <i>Vaccinium vitis-idaea</i> , <i>Dactilina arctica</i> , <i>Aulacomnium sp.</i>
TH6	71° 32' 46.9" N 128° 49' 39.8" E	Typical sedge/ herb/ lichen-moss tundra Dominant species: <i>Carex sp.</i> , <i>Carex aquatilis</i> , <i>Salix sp.</i> , <i>Polygonum sp.</i> , <i>Stellaria sp.</i> , <i>Polemonium coeruleum</i> , <i>Dactylina arctica</i> , <i>Pelygera sp.</i> , <i>Aulacomnium sp.</i> , <i>Hylocomium sp.</i>
TH7	71° 33' 03.0" N 128° 50' 01.0" E	Typical sedge/ lichen-moss tundra Dominant species: <i>Salix sp.</i> , <i>Carex nigra</i> , <i>Polygonum sp.</i> , <i>Pedicularis sp.</i> , <i>Cetraria cucullata</i> , <i>Aulacomnium sp.</i> , <i>Hylocomium sp.</i>
TH8	71° 36' 47.2" N 128° 55' 29.8" E	Typical herbs/ moss-lichen tundra Dominant species: <i>Salix sp.</i> , <i>Betula nana</i> , <i>Carex nigra</i> , <i>Eriophorum vaginatum</i> , <i>Pedicularis sp.</i> , <i>Saxifraga sp.</i> , <i>Tephroseseris tundricola</i> , <i>Cetraria cucullata</i> , <i>Dactilina arctica</i> , <i>Aulacomnium sp.</i> , <i>Hylocomium sp.</i>
TH9	71° 38' 32.6" N 128° 50' 10.3" E	Grass/herbs/moss tundra Dominant species: <i>Carex sp.</i> , <i>Polygonum sp.</i> , <i>Dryas punctata</i> , <i>Saxifraga sp.</i> , <i>Cassiope tetragona</i> , <i>Minuartia sp.</i> , <i>Oxytropis arctica</i> , <i>Vaccinium uliginosum</i> , <i>Cetraria cucullata</i> , <i>Hylocomium sp.</i>
TH10	71° 39' 04.8" N 128° 49' 08.2" E	Typical herbs/moss-lichen tundra Dominant species: <i>Salix sp.</i> , <i>Betula nana</i> , <i>Polygonum sp.</i> , <i>Calamagrostis sp.</i> , <i>Eriophorum sp.</i> , <i>Dactylina arctica</i> , <i>Thamnolia vermicularis</i> , <i>Cetraria cucullata</i> , <i>Hylocomium sp.</i> , <i>Aulacomnium sp.</i>
TH11	71° 38' 56.8" N 128° 47' 24.0" E	Typical sedge/ herbs/ moss tundra Dominant species: <i>Salix sp.</i> , <i>Carex sp.</i> , <i>Carex nigra</i> , <i>Eriophorum sp.</i> , <i>Polygonum sp.</i> , <i>Luzula sp.</i> , <i>Cetraria cucullata</i> , <i>Thamnolia vermicularis</i> , <i>Aulacomnium sp.</i>
TH12	71° 37' 37.8" N 128° 53' 04.5" E	Typical herbs/moss-lichen tundra Dominant species: <i>Salix sp.</i> , <i>Carex nigra</i> , <i>Polygonum viviparum</i> , <i>Polygonum sp.</i> , <i>Luzula sp.</i> , <i>Astragalus sp.</i> , <i>Cassiope tetragona</i> , <i>Cetraria cucullata</i> , <i>Peltigera sp.</i> , <i>Alectoria sp.</i> , <i>Hylocomium sp.</i> , <i>Aulacomnium sp.</i>
TH13	71° 37' 47.4" N 128° 5' 08.9" E	Typical shrubs/ herbs/moss-lichen tundra Dominant species: <i>Salix sp.</i> , <i>Carex sp.</i> , <i>Vaccinium vitis-idaea</i> , <i>Pedicularis sp.</i> , <i>Astragalus sp.</i> , <i>Cetraria cucullata</i> , <i>Hylocomium sp.</i> , <i>Aulacomnium sp.</i>
TH14	71° 38' 58.2" N 128° 50' 51.4" E	Typical herbs/moss-lichen tundra Dominant species: <i>Salix sp.</i> , <i>Carex sp.</i> , <i>Calamagrostis sp.</i> , <i>Stellaria sp.</i> , <i>Pedicularis sp.</i> , <i>Astragalus sp.</i> , <i>Aulacomnium sp.</i>
TH15	71° 37' 32.6" N 128° 50' 17.1" E	Typical sedge/moss tundra Dominant species: <i>Carex sp.</i> , <i>Polygonum viviparum</i> , <i>Polygonum sp.</i> , <i>Eriophorum medium</i> , <i>Dryas punctata</i> , <i>Cetraria cucullata</i> , <i>Thamnolia vermicularis</i> , <i>Peltigera sp.</i> , <i>Aulacomnium sp.</i> , <i>Hylocomium sp.</i>

Table III: Min-max range (numerator) and median values (denominator) of standard soil characteristics of all studied units along the north-south transect.

Sites ID	pH	Texture (%)			C (%)	N (%)	C/N ratio
		Clay	Silt	Sand			
3rd terrace							
3T-1 (n=2 ¹) o	<u>6.0–7.0</u> -	20.0	75.0	4.7	<u>2.50–8.40</u> -	<u>0.20–0.57</u> -	<u>12.6–14.8</u> -
3T-2 (n=2) o	<u>4.0–5.0</u> -	21.0	65.0	14.0	<u>2.50–8.32</u> -	<u>0.15–0.50</u> -	<u>16.6–16.7</u> -
2nd terrace							
2T-1 (n=4 ¹) t	<u>4.0–5.0</u> 5.0	<u>2.0–5.0</u> 4.08	<u>1.0–16.0</u> 4.54	<u>80.0–97.0</u> 91.1	<u>0.14–3.32</u> 1.06	<u>0.01–0.19</u> 0.68	<u>10.4–17.5</u> 15.5
1st terrace							
1T-1 (n=3) t	<u>4.0–5.0</u> 5.0	<u>22.0–27.0</u> 24.4	<u>44.0–46.0</u> 45.0	<u>27.0–34.0</u> 30.5	<u>1.46–8.03</u> 1.85	<u>0.10–0.38</u> 0.13	<u>14.5–21.4</u> 14.8
1T-Rim1 (n=6) t	<u>5.6–6.6</u> 6.2	<u>4.0–9.0</u> 6.6	<u>22.0–52.0</u> 27.9	<u>41.0–73.0</u> 65.5	<u>0.91–4.12</u> 2.80	<u>0.07–0.26</u> 0.18	<u>12.8–20.6</u> 15.2
1T-Ce1 (n=4) h	<u>5.4–5.5</u> 5.5	n.d. ²	n.d.	n.d.	<u>9.64–16.1</u> 12.5	<u>0.26–0.54</u> 0.34	<u>29.9–39.1</u> 36.3
1T-d (n=17) o	<u>5.4–6.9</u> 6.4	n.d.	n.d.	n.d.	<u>2.1–23.4</u> 5.5	<u>0.08–0.21</u> 0.43	<u>18.7–54.7</u> 30.0
High floodplain							
HF-Rim2 (n=5) t	<u>5.6–6.9</u> 6.1	<u>2.0–6.0</u> 3.9	<u>5.0–27.0</u> 21.6	<u>66.0–94.0</u> 74.6	<u>0.30–11.3</u> 1.31	<u>0.03–0.34</u> 0.10	<u>10.4–33.5</u> 13.4
HF-Ce2 (n=4) o	<u>5.8–6.2</u> 5.9	<u>4.0–5.0</u> 4.2	<u>13.0–27.0</u> 20.0	<u>68.0–83.0</u> 75.8	<u>1.12–15.9</u> 6.75	<u>0.07–0.49</u> 0.26	<u>14.2–36.0</u> 20.5
Middle floodplain							
MF-1 (n=8) o	<u>7.0–7.4</u> 7.2	<u>2.0–10.0</u> 4.0	<u>1.0–60.0</u> 10.2	<u>30.0–97.0</u> 85.8	<u>0.30–4.01</u> 1.43	<u>0.03–0.22</u> 0.09	<u>11.3–22.2</u> 14.2
Hinterland							
H-1 (n=5) o	<u>3.0–4.0</u> 4.0	n.d.	n.d.	n.d.	<u>35.0–48.0</u> 40.0	<u>1.51–2.13</u> 1.83	<u>18.9–26.3</u> 19.3
H-2 (n=5) o	<u>3.0–4.0</u> 4.0	<u>10.0–12.0</u> 11.1	<u>29.0–33.0</u> 31.1	<u>55.0–61.0</u> 57.7	<u>1.20–38.6</u> 7.1	<u>0.08–1.05</u> 0.38	<u>15.1–36.9</u> 18.5
H-3 (n=3) o	<u>4.0–6.0</u> 5.0	<u>21.0–22.0</u> 21.5	<u>62.0–63.0</u> 62.6	<u>14.0–17.0</u> 15.9	<u>2.17–17.7</u> 2.21	<u>0.10–0.59</u> 0.12	<u>18.7–30.0</u> 21.7

¹ n – number of the measurements; ² n.d. – not determined; o – Orthel soil suborder, t – Turbel soil suborder, h – Histel soil suborder.

Appendix

Table IV: Min-max range (numerator) and median values (denominator) of standard soil characteristics of all studied units of area around the town Tiksi.

Sites ID	pH	Texture (%)			C (%)	N (%)	C/N ratio
		Clay	Silt	Sand			
Southern sites							
TH1 (n=3 ¹) o	$\frac{5.0-5.2}{5.1}$	$\frac{30.6-32.2}{-}$	$\frac{52.8-61.8}{-}$	$\frac{8.0-16.6}{-}$	$\frac{2.9-18.0}{5.8}$	$\frac{0.27-0.93}{0.45}$	$\frac{10.7-19.3}{12.8}$
TH2 (n=3) t	$\frac{4.4-5.1}{4.8}$	18.0	32.0	50.1	$\frac{3.0-11.3}{6.8}$	$\frac{0.31-0.64}{0.54}$	$\frac{9.9-17.8}{12.7}$
TH6 (n=2) o	$\frac{4.1-5.4}{-}$	17.2	49.1	33.7	$\frac{2.6-11.7}{-}$	$\frac{0.21-0.42}{-}$	$\frac{12.6-27.7}{-}$
TH7 (n=2) o	$\frac{4.6-4.7}{-}$	n.d. ²	n.d.	n.d.	$\frac{11.6-34.3}{-}$	$\frac{0.83-1.41}{-}$	$\frac{12.8-24.3}{-}$
Western sites							
TH3 (n=3 ¹) t	$\frac{5.1-5.7}{5.5}$	26.6	48.7	24.7	$\frac{3.2-30.1}{19.0}$	$\frac{0.28-1.56}{1.34}$	$\frac{11.3-19.3}{14.1}$
TH4 (n=3) t	$\frac{4.8-5.1}{4.8}$	34.6	56.1	9.4	$\frac{6.1-26.3}{16.8}$	$\frac{0.45-1.68}{1.29}$	$\frac{13.0-15.7}{13.7}$
TH5 (n=2) o	$\frac{4.9-5.5}{-}$	n.d.	n.d.	n.d.	$\frac{11.7-21.6}{-}$	$\frac{0.91-1.45}{-}$	$\frac{12.8-14.9}{-}$
Eastern sites							
TH8 (n=3) t	$\frac{5.5-6.4}{5.7}$	31.2	45.9	22.9	$\frac{5.5-28.4}{20.0}$	$\frac{0.44-1.55}{1.45}$	$\frac{12.5-18.3}{13.8}$
TH12 (n=3) t	$\frac{6.4-6.8}{6.8}$	28.4	50.6	21.0	$\frac{7.3-33.4}{17.6}$	$\frac{0.58-1.17}{0.98}$	$\frac{12.6-28.7}{18.0}$
TH13 (n=4) t	$\frac{5.4-6.5}{5.9}$	29.7	54.5	15.9	$\frac{3.3-19.7}{12.0}$	$\frac{0.29-1.21}{0.89}$	$\frac{11.3-16.2}{13.5}$
TH15 (n=3) o	$\frac{6.1-6.6}{6.5}$	n.d.	n.d.	n.d.	$\frac{5.6-40.0}{19.2}$	$\frac{0.52-1.17}{1.06}$	$\frac{10.8-34.3}{18.2}$
Northern sites							
TH9(n=2) o	$\frac{5.9-6.3}{-}$	20.2	43.5	36.2	$\frac{6.2-9.3}{-}$	$\frac{0.49-0.61}{-}$	$\frac{12.7-15.2}{-}$
TH10 (n=3) t	$\frac{4.5-5.2}{4.7}$	n.d.	n.d.	n.d.	$\frac{20.9-33.5}{22.2}$	$\frac{1.28-2.46}{1.30}$	$\frac{13.6-17.0}{16.4}$
TH11 (n=4) t	$\frac{4.1-4.8}{4.5}$	28.0	51.7	20.4	$\frac{6.8-36.8}{26.1}$	$\frac{0.34-1.43}{1.19}$	$\frac{15.0-30.3}{22.3}$
TH14 (n=4) o	$\frac{4.1-5.0}{4.8}$	$\frac{18.6-21.8}{-}$	$\frac{45.3-60.1}{-}$	$\frac{21.3-32.9}{-}$	$\frac{3.8-21.5}{10.2}$	$\frac{0.29-1.23}{0.73}$	$\frac{13.3-17.4}{13.9}$

¹ n – number of the measurements; ² n.d. – not determined; o – Orthel soil suborder, t – Turbel soil suborder.

Table V: Min-max range (numerator) and median values (denominator) of the trace metals in mg kg⁻¹ determined in the soils of investigated units in northern Siberia and quantification limits.

Name Quantif. limit	Third terrace		Second terrace		First terrace	
	3T-1 (n=2 ¹)	3T-2 (n=2)	2T-1 (n=4)	1T-1 (n=3)	1T-Rim1 (n=6)	1T-Ce1 (n=4)
As 0.1	<u>5.09 – 6.80</u> -	<u>4.78 – 5.12</u> -	<u>1.22 – 1.36</u> 1.29	<u>5.01 – 12.1</u> 11.3	<u>2.09 – 10.0</u> 2.95	<u>3.18 – 3.82</u> 3.35
Cd 0.01	<u>0.03 – 0.06</u> -	<u><QL – <QL</u> -	<u><QL – 0.36</u> 0.01	<u><QL – 0.05</u> <QL	<u>0.03 – 0.07</u> 0.05	<u>0.03 – 0.06</u> 0.04
Co 0.06	<u>19.1 – 21.0</u> -	<u>20.9 – 26.3</u> -	<u>11.9 – 28.4</u> 14.6	<u>23.1 – 28.4</u> 24.5	<u>40.0 – 146</u> 48.8	<u>28.5 – 79.5</u> 43.5
Cu 0.04	<u>9.69 – 17.0</u> -	<u>8.13 – 10.9</u> -	<u>0.6 – 6.85</u> 1.0	<u>7.17 – 28.2</u> 7.21	<u>2.74 – 7.91</u> 4.51	<u>9.70 – 12.0</u> 11.0
Fe 8.0	<u>33620 – 43850</u> -	<u>22330 – 35770</u> -	<u>5280 – 8000</u> 6300	<u>22200 – 49420</u> 44100	<u>17800 – 41200</u> 18900	<u>17000 – 21000</u> 18800
Hg 0.01	<u>0.011 – 0.016</u> -	<u>0.022 – 0.024</u> -	<u><QL – 0.012</u> 0.010	<u>0.01 – 0.022</u> 0.013	<u>0.016 – 0.037</u> 0.018	<u><QL – 0.019</u> 0.010
Mn 3.3	<u>585 – 627</u> -	<u>397 – 721</u> -	<u>142 – 186</u> 158	<u>173 – 301</u> 237	<u>224 – 1206</u> 334	<u>143 – 481</u> 187
Ni 0.1	<u>27.4 – 32.9</u> -	<u>23.4 – 24.5</u> -	<u>4.89 – 9.94</u> 5.12	<u>21.0 – 32.0</u> 28.3	<u>11.2 – 23.3</u> 21.7	<u>17.1 – 24.1</u> 18.5
Pb 0.3	<u>9.37 – 9.57</u> -	<u>7.70 – 9.22</u> -	<u>2.14 – 3.69</u> 2.41	<u>6.58 – 9.78</u> 9.16	<u>5.02 – 7.37</u> 6.84	<u>5.21 – 31.2</u> 7.55
Zn 1.3	<u>70.3 – 76.4</u> -	<u>52.2 – 57.0</u> -	<u>12.1 – 23.9</u> 12.4	<u>60.9 – 73.9</u> 72.8	<u>43.1 – 60.6</u> 59.3	<u>34.9 – 59.2</u> 49.0
Name detection limit	High floodplain		Middle floodplain		Hinterland	
	HF-Rim2 (n=5)	HF-Ce2 (n=4)	MF-1 (n=8)	H-1 (n=5)	H-2 (n=5)	H-3 (n=3)
As 0.1	<u>2.24 – 3.69</u> 3.15	<u>2.06 – 3.95</u> 2.80	<u>2.94 – 6.74</u> 4.99	<u>1.63 – 3.90</u> 3.13	<u>2.68 – 8.06</u> 4.75	<u>3.38 – 5.05</u> 4.48
Cd 0.01	<u>0.02 – 0.04</u> 0.02	<u>0.01 – 0.08</u> 0.04	<u>0.02 – 0.11</u> 0.05	<u>0.02 – 0.09</u> 0.09	<u><QL – 0.24</u> <QL	<u><QL – 0.18</u> <QL
Co 0.06	<u>20.2 – 54.7</u> 40.9	<u>30.0 – 69.4</u> 40.2	<u>52.7 – 110</u> 92.1	<u>10.6 – 18.7</u> 14.1	<u>10.9 – 22.8</u> 11.9	<u>19.4 – 23.5</u> 21.6
Cu 0.04	<u>0.95 – 8.30</u> 4.49	<u>2.57 – 14.0</u> 7.81	<u>1.02 – 9.80</u> 3.43	<u>11.9 – 47.0</u> 20.6	<u>1.48 – 11.2</u> 8.09	<u>16.0 – 21.9</u> 17.8
Fe 8.0	<u>10700 – 18200</u> 15500	<u>12000 – 20000</u> 15650	<u>13000 – 38000</u> 25750	<u>8430 – 19780</u> 13210	<u>3190 – 50270</u> 17680	<u>25820 – 47050</u> 44850
Hg 0.01	<u><QL – 0.019</u> <QL	<u>0.010 – 0.017</u> 0.012	<u>0.015 – 0.050</u> 0.027	<u><QL – 0.017</u> 0.01	<u><QL – 0.049</u> 0.011	<u><QL – 0.019</u> <QL
Mn 3.3	<u>143 – 1385</u> 271	<u>139 – 633</u> 260	<u>185 – 503</u> 340	<u>10.93 – 78.6</u> 23.0	<u>65.5 – 230</u> 107	<u>202 – 342</u> 322
Ni 0.1	<u>11.7 – 20.2</u> 17.2	<u>12.3 – 23.7</u> 18.2	<u>11.8 – 32.6</u> 20.1	<u>9.10 – 21.4</u> 19.7	<u>7.15 – 23.2</u> 12.0	<u>16.2 – 27.1</u> 25.4
Pb 0.3	<u>3.55 – 5.44</u> 4.69	<u>4.00 – 6.63</u> 5.27	<u>4.60 – 9.96</u> 6.62	<u>2.29 – 12.6</u> 4.33	<u>3.01 – 6.79</u> 4.83	<u>10.0 – 13.3</u> 13.1
Zn 1.3	<u>23.9 – 47.5</u> 39.5	<u>29.9 – 55.0</u> 37.8	<u>28.3 – 84.0</u> 55.1	<u>14.4 – 28.7</u> 17.4	<u>24.8 – 72.9</u> 39.1	<u>74.3 – 81.0</u> 75.1

¹ n - number of the measurements

Appendix

Table VI: Min-max range (numerator) and median values (denominator) of the trace metals in mg kg⁻¹ determined in the soils of investigated units in the area around the settlement Tiksi.

	Element mg kg ⁻¹								
	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Southern sites									
TH1 (n=3)	<u>8.6 - 11.7</u> 10.6	<u>0.03 - 0.27</u> 0.05	<u>16.2 - 57.9</u> 32.2	<u>7.3 - 17.2</u> 9.8	<u>27834 - 43082</u> 34036	<u>85 - 2666</u> 374	<u>39.1 - 50.1</u> 42.4	<u>7.9 - 21.8</u> 20.2	<u>80.8 - 127</u> 90
TH2 (n=3)	<u>10.3 - 20.5</u> 12.6	<u>0.05 - 0.3</u> 0.06	<u>15.0 - 24.0</u> 15.5	<u>7.8 - 9.3</u> 9.3	<u>27834 - 40773</u> 32343	<u>284 - 464</u> 412	<u>25.5 - 41.8</u> 32.8	<u>17.9 - 22.8</u> 21.6	<u>92.3 - 116</u> 99.4
TH6 (n=2)	<u>8.8 - 10.8</u> -	<u>0.06 - 0.1</u> -	<u>22.1 - 26.6</u> -	<u>6.7 - 7.0</u> -	<u>17962 - 33420</u> -	<u>316 - 496</u> -	<u>17.4 - 24.3</u> -	<u>11.4 - 20.0</u> -	<u>81 - 98.1</u> -
TH7 (n=2)	<u>5.2 - 11.4</u> -	<u>0.07 - 0.3</u> -	<u>63.6 - 82.9</u> -	<u>10.4 - 11.4</u> -	<u>20403 - 22446</u> -	<u>348 - 5374</u> -	<u>21.2 - 34.2</u> -	<u>10.5 - 17.2</u> -	<u>56.8 - 142</u> -
Western sites									
TH3 (n=3)	<u>6.2 - 13.4</u> 7.4	<u>0.02 - 0.71</u> 0.17	<u>13.6 - 30.3</u> 16.0	<u>5.6 - 22.7</u> 18.0	<u>13765 - 37899</u> 17937	<u>374 - 2306</u> 1062	<u>21.2 - 55.4</u> 33.9	<u>12.5 - 22.1</u> 15.1	<u>74.8 - 218</u> 80.5
TH4 (n=3)	<u>7.4 - 8.2</u> 8.0	<u>0.06 - 0.34</u> 0.13	<u>25.7 - 49.2</u> 32.5	<u>9.5 - 19.1</u> 18.6	<u>22068 - 28438</u> 23525	<u>174 - 2514</u> 338	<u>23.3 - 45.1</u> 30.2	<u>18.6 - 23.3</u> 22.0	<u>54 - 71.6</u> 62.8
TH5 (n=3)	<u>3.7 - 14.5</u> 9.1	<u>0.12 - 0.21</u> 0.16	<u>19.6 - 50.9</u> 35.3	<u>17.9 - 20.0</u> 19.0	<u>12722 - 30707</u> 21715	<u>185 - 2236</u> 1211	<u>28.6 - 40.4</u> 34.5	<u>24.0 - 25.2</u> 24.6	<u>52.6 - 82.9</u> 67.8
Eastern sites									
TH8 (n=3)	<u>4.8 - 8.0</u> 5.5	<u>0.12 - 0.35</u> 0.17	<u>13.1 - 20.6</u> 18.2	<u>17.2 - 25.2</u> 18.1	<u>13605 - 30011</u> 16753	<u>184 - 1889</u> 394	<u>28.2 - 34.3</u> 30.1	<u>14.0 - 26.8</u> 16.7	<u>53.7 - 166</u> 108
TH12 (n=3)	<u>6.0 - 11.4</u> 7.6	<u>0.10 - 0.40</u> 0.33	<u>19.0 - 65.0</u> 30.5	<u>11.2 - 16.6</u> 15.2	<u>12098 - 33972</u> 25590	<u>659 - 3433</u> 1139	<u>12.0 - 33.1</u> 23.9	<u>14.8 - 20.9</u> 17.4	<u>94 - 106</u> 101
TH13 (n=4)	<u>5.7 - 10.6</u> 8.4	<u>0.05 - 0.32</u> 0.24	<u>23.9 - 117</u> 29.6	<u>9.2 - 20.3</u> 13.3	<u>20658 - 34745</u> 26179	<u>108 - 5242</u> 2146	<u>15.7 - 31.2</u> 28.1	<u>7.2 - 18.1</u> 15.3	<u>69.7 - 204</u> 156.5
TH15 (n=3)	<u>2.3 - 10.1</u> 6.1	<u>0.10 - 0.50</u> 0.42	<u>12.3 - 60.0</u> 59.2	<u>11.2 - 34.8</u> 32.2	<u>6494 - 29057</u> 22623	<u>288 - 1210</u> 429	<u>21.0 - 36.8</u> 23.6	<u>6.7 - 28.1</u> 19.2	<u>63.5 - 91.7</u> 90.6
Northern sites									
TH9 (n=2)	<u>11.3 - 14.4</u> -	<u>0.10 - 0.26</u> -	<u>22.2 - 24.8</u> -	<u>10.7 - 11.4</u> -	<u>24590 - 35620</u> -	<u>687 - 947</u> -	<u>24.1 - 28.2</u> -	<u>27.6 - 29.7</u> -	<u>114 - 121</u> -
TH10 (n=3)	<u>3.1 - 5.5</u> 3.6	<u>0.10 - 0.60</u> 0.15	<u>12.0 - 17.4</u> 14.8	<u>13.9 - 26.9</u> 17.2	<u>9102 - 14080</u> 13222	<u>13 - 1826</u> 110	<u>0.9 - 15.9</u> 11.8	<u>14.7 - 21.5</u> 18.7	<u>16.3 - 440</u> 28.6
TH11 (n=4)	<u>4.6 - 13.8</u> 5.4	<u>0.05 - 0.63</u> 0.15	<u>10.3 - 53.2</u> 53.2	<u>10.8 - 20.3</u> 16.0	<u>17083 - 56084</u> 20838	<u>53 - 2321</u> 484	<u>8.2 - 27.4</u> 16.4	<u>8.7 - 21.0</u> 17.9	<u>32.6 - 69.9</u> 45.9
TH14 (n=4)	<u>4.8 - 12.4</u> 9.2	<u>0.04 - 0.68</u> 0.17	<u>17.0 - 32.2</u> 26.0	<u>9.2 - 39.0</u> 21.9	<u>18618 - 27874</u> 26784	<u>47 - 453</u> 152	<u>17.3 - 35.8</u> 24.5	<u>19.8 - 38.9</u> 24.4	<u>50.9 - 129</u> 66.7

Table VII: Min-max range (numerator) and median values (denominator) of the trace metal concentrations reported for soil types of Eastern Barents region, Baltic region, the Lower Lena River area, northeastern Siberia and western Siberia.

Soil type	Data source	Element mg kg ⁻¹ dw				
		As	Cd	Co	Cu	Fe
Gleysols*		<u>0.44 – 12.0</u> 4.50	<u>0.005 – 0.292</u> 0.063	<u>1.38 – 52.8</u> 8.31	<u>1.03 – 59.3</u> 9.42	<u>2690 – 47200</u> 16300
Histosols	1	<u>0.05 – 30.8</u> 1.04	<u>0.005 – 0.33</u> 0.027	<u>0.5 0 – 33.6</u> 4.70	<u>0.50 – 152</u> 8.80	<u>259 – 77000</u> 11300
Fluvisols		<u>0.05 – 15.1</u> 1.73	<u>0.005 – 0.34</u> 0.026	<u>0.50 – 23.0</u> 7.28	<u>0.50 – 28.0</u> 13.0	<u>646 – 34200</u> 13000
Organic soil layer	2	<u>0.25 – 17.8</u> 1.56	<u>0.08 – 3.18</u> 0.40	<u>0.29 – 12.6</u> 1.16	<u>2.85 – 87.3</u> 7.60	<u>767 – 21400</u> 2890
Tundra gleysols	3	<u>0.02 – 0.78</u> 0.22	<u>0.03 – 0.40</u> 0.12	—	<u>0.72 – 5.02</u> 2.50	—
Hydric soils		—	<u>0.05 – 0.81</u> -	—	<u>2.70 – 63.0</u> -	—
Sedge-moss peat	4	—	<u>0.03 – 0.48</u> -	—	<u>3.0 – 62.0</u> -	—
Hydric soils		—	<u>0.05 – 56.0</u> -	—	<u>1.70 – 664</u> -	—
Polygonal bog peat	5	—	<u>0.05 – 64.0</u> -	—	<u>1.50- 442</u> -	—
Organic soil layer	6	—	—	—	<u>2.0 – 18.0</u> -	<u>500 – 17000</u> -
Organic soil layer	7	—	—	—	<u>3.9 – 24.0</u> -	—

Soil type	Data source	Element mg kg ⁻¹ dw				
		Hg	Mn	Ni	Pb	Zn
Gleysols*		—	<u>31.1 – 5020</u> 377	<u>2.82 – 682</u> 20.1	<u>0.52 – 8.55</u> 3.29	<u>0.50 – 87.9</u> 30.6
Histosols	1	—	<u>3.18 – 3280</u> 122	<u>1.00 – 49.5</u> 11.3	<u>0.30 – 15.8</u> 1.81	<u>0.50 – 93.6</u> 15.8
Fluvisols		—	<u>11.2 – 3480</u> 274	<u>1.00 – 73.4</u> 17.5	<u>0.43 – 8.88</u> 2.99	<u>2.65 – 65.5</u> 26.0
Organic soil layer	2	<u>0.04 – 0.42</u> 0.20	<u>23.6 – 4880</u> 265	<u>1.54 – 131</u> 5.06	<u>6.52 – 361</u> 31.1	<u>7.70 – 90.9</u> 20.0
Tundra gleysols	3	<u>0.01 – 0.04</u> 0.02	—	<u>0.72 – 4.96</u> 2.60	—	<u>6.80 – 18.9</u> 13.0
Hydric soils		—	—	—	<u>1.8 0 – 44.0</u> -	<u>4.40 – 137</u> -
Sedge-moss peat	4	—	—	—	<u>1.90 – 23.0</u> -	<u>4.00 – 96.0</u> -
Hydric soils		—	—	—	<u>1.90 – 288</u> -	<u>4.6 0 – 920</u> -
Polygonal bog peat	5	—	—	—	<u>1.5 – 274</u> -	<u>12.0 – 878</u> -
Organic soil layer	6	<u>0.01 – 0.17</u> —	<u>4.0 – 820</u> —	—	<u>1.0 – 24.0</u> -	<u>5.0 – 48.0</u> -
Organic soil layer	7	<u>0.09 – 0.29</u> -	<u>9.0 – 123</u> -	—	<u>16.0 – 29.0</u> -	<u>43.0 – 81.0</u> -

1 – Salminen et al (2004), C-horizon, Eastern Barents region, aqua regia extraction;

2 – Salminen et al (2011), Eastern Baltic region, total extraction;

3 – Rovinsky et al (1995), Kyusur, the Lower Lena River area; **denominator – mean value**

4 – Zhulidov et al (1997a), pristine wetlands of the North-Eastern Siberia;

5 – Zhulidov et al (1997b), wetlands in the Western Siberia tundra zone, minimum values are reported for background area, maximum values are reported for areas exposed to anthropogenic pollution;

6 – Walker (2012), pristine soils from the sub-Arctic region of Labrador, Canada;

7 – Reimann et al (2009), Norway.

* – according to WRB soil classification (FAO, 2006).

Appendix

Table VIII: Element composition of plant species (min-max - numerator, median - denominator) in the Lena River Delta region and the Tiksi area (in mg kg⁻¹ dw).

Vegetation species	Element concentration (mg kg ⁻¹ dw)					
	Cu	Fe	Mn	Ni	Pb	Zn
<i>Lena River Delta</i>						
Mosses (n = 13)	<u>3.32 – 10.0</u> 7.02	<u>5420 – 21049</u> 11152	<u>108 – 280</u> 167	<u>4.82 – 12.3</u> 9.28	<u>2.19 – 4.83</u> 3.46	<u>14.1 – 36.2</u> 24.0
Lichens (n = 7)	<u>2.37 – 10.8</u> 3.75	<u>305 – 3264</u> 2338	<u>48.0 – 87.0</u> 75.0	<u>1.86 – 11.7</u> 3.80	<u>1.24 – 2.03</u> 1.67	<u>16.9 – 25.8</u> 20.9
bush (n = 3)	<u>3.41 – 5.04</u> 3.67	<u>208 – 410</u> 252	<u>750 – 1016</u> 962	<u>0.35 – 0.79</u> 0.77	<u>0.37 – 3.81</u> 0.45	<u>18.6 – 25.3</u> 25.2
<i>Tiksi</i>						
Mosses (n = 2)	<u>4.07 – 5.34</u> –	<u>1678 – 1977</u> –	<u>282 – 372</u> –	<u>6.38 – 15.2</u> –	<u>1.76 – 3.26</u> –	<u>78.6 – 82.5</u> –
Lichens (n = 10)	<u>1.43 – 4.20</u> 2.80	<u>85.0 – 5850</u> 340	<u>18.0 – 556</u> 42.6	<u>0.79 – 10.9</u> 2.43	<u>0.97 – 7.77</u> 1.76	<u>11.9 – 60.5</u> 17.5
bush (n = 3)	<u>5.39 – 7.53</u> 5.45	<u>186 – 242</u> 206	<u>1730 – 2810</u> 2173	<u>1.58 – 3.46</u> 2.08	<u>0.55 – 0.69</u> 0.56	<u>35.7 – 49.4</u> 49.4
Dobrovol'sky (2003)*	8.0	–	205	2.0	1.25	30.0
Evseev (2003)**	3.0	800	–	4.0	4.0	20.0

* Average element concentration in dry phytomass worldwide;

** Background concentrations in mosses for areas of northern Eurasia.

Table IX: Ranges of the element concentrations (mg kg⁻¹ dw) in individual vegetation groups from earlier studies of areas in the Arctic and sub-Arctic regions.

Species	Data source	Cu	Fe	Mn	Ni	Pb	Zn
Mosses							
<i>Hylocomium splendens</i>	1	2.60 – 83.0	535 - 7870	13.5 – 256	1.16 – 56.7	1.41 – 3.27	7.97 – 44.1
	2	2.6 – 214	47 - 5140	–	0.97 - 396	0.8 – 29.4	12 – 82
	4	5.50 – 6.30	530 – 890	270 – 510	2.6 – 2.80	11 – 15	42.0 – 72.0
	11	2.63 – 3.55	46 - 5140	28.5 - 1170	0.96 - 396	0.84 – 29.4	11.7 – 81.9
<i>Hylocomium splendens</i>	5	3.07 – 9.09	–	–	2.31 – 4.81	5.09 – 7.99	–
	6	3.48 – 33.0	–	28.2 – 282	–	0.75 – 26.6	10.5 – 65.9
<i>Hylocomium splendens</i>	12	3.31 – 5.23	–	–	1.91 – 4.13	0.93 – 1.97	9.06 – 24.8
Lichens							
<i>C. cucullata</i>	1	1.10 – 12.8	290 - 1000	8.45 - 134	0.83 – 10.2	0.78 – 5.80	9.70 – 29.6
	6	1.79 – 36.8	–	3.91 – 244	–	0.16 – 6.1	3.40 – 68.2
<i>C. Stellaris</i>	7	1.74 – 1.92	253 - 308	33.7 – 40.1	0.81 – 0.91	4.1 – 4.9	16.3 – 18.7
Bushes							
<i>Vaccinium vitis-idaea</i>	3	6.0 – 53.0	–	–	2.0 - 97	1.1 – 2.3	–
	8	4.0 – 8.0	0.10-4.0	38.0 – 235	3.0 – 10.0	–	10.0 – 18.0
	9*	–	–	–	58	2.1	1.6
	10*	2.59	61.6	451	1.98	–	–

1 – Allen-Gil et al (2003). Taimyr peninsula;

2 – Åyräs et al (1997). Finland, Norway, and Russia (Kola peninsula);

3 – Barcan et al (1998). Kola Peninsula (minimum element concentrations determined for species collected at a distance 83 km from the Smelter, maximum element contents determined in plants at 4 km distance from the Smelter (Monchegorsk);

4 – Berg & Steinnes (1997). Norwegian station (Nordmoen);

5 – Grodzhinska et al (1991). Southern Spitsbergen;

6 – Jozwik (1990). Bellsund area, Spitsbergen; Ranges are given for the species groups;

7 – Moskovchenko & Valeeva (2006). North-Western Siberia;

8 – Opekunova et al, 2007 (Kola Peninsula Background area 40-45 km to the south from Monchegorsk);

9* – Pöykiö et al (2005). Background area, Northern Finland; Berries of *Vaccinium vitis-idaea*;

10*– Ramenskaya (1974) Background area. Kola Peninsula;

11 – Reimann et al (2001). Central Barents Region, Finland, Norway, and Russia;

12 – Wilkie & La Farge (2011). Piper pass - 2007, Canada;

* - Mean concentration