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Organic matter in permafrost-affected soils as affected by soil forming processes and vegetation in the Arctic and Antarctica

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Content

Summary

Soils represent the largest terrestrial carbon pool and especially permafrost-affected soils contribute noteworthy to the global carbon (C) budget as they contain large amounts of organic matter (OM). Permafrost covers about 17 % of the exposed land surface and is defined as ground (soil, rock, sediment) that is frozen for at least two consecutive years. Recent estimations amount the soil organic C (SOC) stock in permafrost-affected soils to 1,014 Pg down to a depth of three meters. And while more than 98 % of terrestrial permafrost are located in the Northern Hemisphere with Arctic soils contributing immensely to the global C budget, the organic C (OC) stocks of soils from Antarctica are marginal.

The factors for soil development in general are climate, biota, relief, parent material, and time with a clear dominance of parent material and climate in polar regions, as cold temperatures retard biological and chemical processes and limit vegetation growth. The presence of permafrost itself has an explicit impact on soil development with thawing and freezing cycles of the active layer that facilitate geomorphologic processes like cryoturbation, frost heaving, and cryoclastic weathering. Biota in the polar regions are adapted to the hostile conditions with low temperatures, large temperature amplitudes, and darkness during the polar night that restrict growing seasons. While the climatic and geogenic differences result in fundamentally different stages of soil development in Antarctica and most parts of the Arctic, similar pedogenic processes are active in both polar regions, e.g. OM accumulation, redoximorphism, or desert pavement formation.

Global warming affects the whole planet Earth, but both the Arctic and Antarctica, especially maritime Antarctica, face a much more pronounced impact by climate change as they heat much faster than other regions and experience frequent temperature records. As climate has governed soil development for millennia in these regions, ongoing warming is about to fundamentally change soil processes. It is essential to obtain a deeper understanding of the current state of permafrost-affected soils, their properties and the properties of their OM to decode their soil processes and probable consequences of warming. Therefore, the scope of this thesis was to investigate permafrost-affected soils from the Arctic and Antarctica with focus on their soil OM (SOM) pools. The separation of different SOM pools enables the examination of different stabilization mechanisms that dominate the respective fractions. In addition, it allows to obtain more detailed information on the constituents of the soil than the exclusive investigation of bulk soil samples. Applying several wet-chemical and spectroscopic methods, I aimed at obtaining detailed information on the characteristics of the SOM of permafrost-affected soils and at getting insights into the mechanisms governing its buildup and distribution. To accomplish this, three different projects were conducted covering the range from initial soil development in the pristine environment of maritime Antarctica to the peak of SOC storage in permafrost-affected soils rich in OM in the Siberian Arctic:

I. Initial soil development in maritime Antarctica

Soils from a gradient at a freshwater lake on James Ross Island in maritime Antarctica were explored to obtain insights in the interconnected development of soils and biological soil crusts (BSC). The gradient ranged from the lake sediment to rather terrestrial habitats covered with BSC. The aim of this study was to understand the effect of water availability on the formation of SOM and microbial communities. To achieve this aim, bulk soils were analyzed and fractionated, SOM fractions were investigated and in addition, lipid biomarkers were extracted and evaluated.

II. Vegetation and soil development in maritime Antarctica

The core objective of this study was to assess the impact of vegetation on soil development and OM buildup in maritime Antarctica. Therefore, vegetation-covered and vegetation-free soils from two islands (James Ross Island, King George Island) in maritime Antarctica were analyzed for their basic soil properties and fractionated according to density and grain size to study the distribution of soil C within different SOM fractions.

III. The state of SOM in the Siberian high Arctic

In the third study, I aimed at elucidating the depth distribution of SOM fractions together with their chemical composition to better understand soil C storage in very OC rich Arctic soils. Soil cores from Samoylov Island in the Lena River delta in the Siberian Arctic were investigated to receive information on the depth distribution of SOM and its characteristics. Bulk soil samples were separated to obtain particulate and mineral-associated OM fractions for detailed analyses of their chemical composition

Throughout all chapters of this dissertation, I separated SOM fractions by density and grain size and investigated their distribution and chemical composition. The soils from maritime Antarctica (Study I and II) were dominated by coarse fractions and contained only little particulate OM (POM). In both studies, I examined the horizontal distribution of SOM. In Study I, the more terrestrial sites covered with BSC contained more POM than the lake sediment and the regularly flooded area, pointing to a basic SOM buildup under BSC in undisturbed conditions. The vegetation-free soils in Study II contained significant less large POM fractions than the vegetation-covered soils, revealing the impact of the scarce Antarctic vegetation on the buildup of SOM. The chemical composition of the respective POM fractions in Study II resembled the chemical composition of the input litter, whereas the clay-sized mineral-associated OM (MAOM) from vegetation-free soils contained clearly more aromatic compounds than the one from vegetation-covered soils. The Arctic soils in Study III showed overall a very heterogeneous distribution of SOM fractions regarding both differences between the individual soil cores and the depth distribution. The soils revealed the impact of cryoturbation with deep layers dominated by POM that were located between layers dominated by MAOM. The chemical composition of the large POM fractions with a strong dominance of O/N alkyl C compounds differed clearly from the one of the clay-sized MAOM fractions with larger proportions of carboxyl and alkyl C compounds, while the small POM fractions turned out to be the linking element between large POM and MAOM fractions.

In Study I, I demonstrate that BSC and soils develop closely interwoven in the pristine environment close to a freshwater lake on James Ross Island, an arid polar island in maritime Antarctica. Investigating a gradient from the lake sediment of the freshwater lake towards terrestrial habitats covered with BSC, I show that the development of BSC and soils is disturbed and hampered in both the lake sediment and the regularly flooded area, but that SOM accrual and soil development increase with distance to the lake and decrease again after reaching a peak. This peak of soil formation is characterized by the highest C and POM contents within the studied gradient as well as significant adaption mechanisms within the BSC, *e.g.* in the form of membrane rigidification by an increased production of sitosterol. Therefore, I conclude first, that the availability of freshwater is the major regulating factor for the co-evolution of soils and BSC under the arid polar climate regime and second, that disturbance by regular flooding impedes this evolution.

In Study II, I showed that the scarce vegetation on polar islands in maritime Antarctica has a clear impact on both SOM distribution and soil development. I compared soils from James Ross Island and King George Island with different climate regimes and with a differently structured vegetation. On both islands, I found more C and nitrogen (N) as well as more POM in vegetation-covered soils. In addition, clay-sized MAOM of these soils contained more rather labile compounds The polar maritime climate on King George Island allows for the growth of vascular plants and I suppose that the belowground input of OM by the roots of these plants is decisive for the more pronounced SOM buildup. The climate of James Ross Island is arid polar and restricts the vegetation to cryptogams that grow in mat-like structures. Therefore, I presume that these structures act like retention elements for OM. I demonstrated that the patchy vegetation can act as hot spot for biogeochemical processes in these soils and that vegetation patches foster both the buildup of SOM and the presence of bioavailable organic compounds that in turn are able to enhance microbial activity.

Study III focused on OM-rich soil cores from Samoylov Island in the Siberian Arctic. The key finding of my investigation of these soils was that the fractions that dominate the C stock were at the same time the most labile ones. All POM fractions together stored about 80 % of the C, whereas about 50 % of the C stock was present in the large free POM fractions. The SOC in these fractions consisted of rather labile compounds and has been so far mainly preserved by the cold temperatures. Ongoing warming and thawing will most likely increase its bioavailability and therewith accelerate its decomposition. In this scenario, small POM and clay-sized MAOM fractions with an assumed low bioavailability will presumably dominate the C stock in a warmer future.

This dissertation covers soils from both the Arctic and Antarctica and gives insight into the huge differences between the hardly developed soils from maritime Antarctica (Study I and II) with very low amounts of SOM and the soil cores from the Siberian Arctic (Study III) that show both a very advanced soil development and large OM reservoirs. Soil development in Antarctica is still on an initial stage and so far, it is not clear which turn it will take: Increasing temperatures might lead to a propagation of vegetation and thereby – as demonstrated in Study II – to an acceleration of soil processes. Yet, if the warming comes with increasing aridity, vegetation and soils might become even more barren in the future as the availability of freshwater is key for the intertwined development of soils and BSC as shown in Study I. For Arctic soils rich in OM, like the soils investigated in Study III, ongoing warming will most probably lead to a loss of parts of the immense C stocks as these are dominated by compounds that are most likely highly bioavailable once preservation by freezing ends. However, along with this evolution will come most likely a shift in the C stock towards small POM and clay-sized MAOM fractions as these fractions are dominated by more stable C compounds.

As soils, soil biota, and vegetation are highly adapted to harsh conditions in the Arctic and maritime Antarctica, they face fundamental changes under warming conditions. Thus, with this thesis I provide important information on the current status of the examined soils and their SOM that enables the tracking of alterations caused by climate change and other anthropogenic interference in the future.

Zusammenfassung

Böden sind der größte terrestrische Kohlenstoffspeicher. Vor allem Permafrostböden tragen in einem beachtlichen Maß zum globalen Kohlenstoffhaushalt bei, da in ihnen große Mengen organischen Materials (OM) konserviert sind. Permafrost befindet sich auf ca. 17 % der gesamten Landoberfläche. Bei Permafrost handelt es sich um gefrorenen Untergrund (Boden, Fels, Sediment), der mindestens zwei aufeinanderfolgende Jahre hindurch gefroren ist. Die Menge an organischem Kohlenstoff in Permafrostböden bis in eine Tiefe von drei Metern wird auf etwa 1.014 Pg geschätzt. Während sich mehr als 98 % des terrestrischen Permafrosts in der nördlichen Hemisphäre befinden und arktische Böden in hohem Maße zum globalen Kohlenstoffhaushalt beitragen, sind die Vorräte an organischem Kohlenstoff in Böden der Antarktis unbedeutend.

Im Allgemeinen sind die Faktoren für Bodenbildung Klima, Biota, Relief, Ausgangsmaterial und Zeit, wobei in Polargebieten Ausgangsmaterial und Klima deutlich dominieren. Hier verlangsamen niedrige Temperaturen biologische und chemische Prozesse und schränken das Wachstum von Vegetation ein. Permafrost selbst hat einen deutlichen Einfluss auf die Bodenbildung, da die Forst- und Tauzyklen der Auftauzone geomorphologischen Prozesse wie Kryoturbation, Frosthebungen und kryoklastische Verwitterung ermöglichen. Lebewesen in den polaren Gebieten sind an die widrigen Bedingungen mit niedrigen Temperaturen, immensen Temperaturunterschieden und Dunkelheit während der Polarnächte, die die Vegetationsperiode stark begrenzt, angepasst. Während die klimatischen und geogenen Unterschiede zu unterschiedlichen Entwicklungsstufen der Böden in der Antarktis und großen Teilen der Arktis führten, sind in beiden Polargebieten dennoch ähnliche bodenbildende Prozesse, z. B. die Akkumulation von OM, Redoximorphose oder die Entstehung von Wüstenmosaik, aktiv.

Der Klimawandel betrifft die gesamte Erde, aber sowohl Arktis als auch Antarktis, besonders die maritime Antarktis, sind in besonderem Maße von den Folgen der globalen Erwärmung betroffen. Diese Regionen erwärmen sich deutlich schneller als andere Gebiete, was regelmäßig neue Temperaturrekorde zur Folge hat. Da das Klima über Jahrtausende hinweg der maßgebliche bodenbildende Faktor in diesen Gebieten war, ist die Erwärmung nun im Begriff, Bodenprozesse grundlegend zu verändern. Es ist daher notwendig, ein tiefgreifendes Verständnis für den derzeitigen Zustand von Permafrostböden, ihren Eigenschaften und den Eigenschaften ihres OM zu bekommen, um die Prozesse in diesen Böden und die

wahrscheinlichen Folgen der Erwärmung zu verstehen. Ziel dieser Arbeit war es daher, Permafrostböden aus Arktis und Antarktis hinsichtlich ihrer OM-Speicher zu untersuchen. Die Trennung verschiedener OM-Speicher mittels Fraktionierung gemäß Dichte und Korngröße erlaubt es, die verschiedenen Stabilisierungs-mechanismen, die die entsprechenden Speicher dominieren, zu analysieren. Zudem ermöglicht sie es, detailliertere Informationen über die Bestandteile des Bodens zu erlangen als es durch die ausschließliche Untersuchung von Gesamtbodenproben möglich ist. Der Einsatz verschiedener nasschemischer und spektroskopischer Methoden zielte darauf ab, detaillierte Informationen über die Eigenschaften des OM in Permafrostböden und Einblicke in die Mechanismen, die den Aufbau und die Verteilung des OM regulieren, zu erhalten. Um dies zu erreichen, wurden drei verschiedene Studien durchgeführt, die die Spanne von initialer Bodenbildung in der nahezu unberührten maritimen Antarktis bis zum Höchstwert der Speicherung von organischem Kohlenstoff in äußerst OM-reichen Permafrostböden der Sibirischen Arktis abdecken:

I. Initiale Bodenbildung in der maritimen Antarktis

Auf James Ross Island in der maritimen Antarktis wurden Böden entlang eines Gradienten in der Nähe eines Süßwassersees untersucht, um Einblicke in die eng miteinander verwobene Entwicklung von Böden und biologischen Bodenkrusten zu erhalten. Der Gradient begann im Seesediment und erstreckte sich hin zu terrestrischen, von biologischen Bodenkrusten bedeckten Bereichen. Ziel dieser Studie war es, den Effekt von Wasserverfügbarkeit auf die Bildung von organischer Bodensubstanz und mikrobielle Gemeinschaften zu verstehen. Hierzu wurden Gesamtbodenproben untersucht und fraktioniert sowie die entsprechenden OM-Fraktionen analysiert und zusätzlich Lipid-Biomarker extrahiert und ausgewertet.

II. Vegetation und Bodenbildung in der maritimen Antarktis

Kernziel dieser Studie war es, den Einfluss von Vegetation auf Bodenentwicklung und Aufbau von OM in der maritimen Antarktis zu ermitteln. Dazu wurden Böden mit Vegetation und vegetationsfreie Böden von zwei Inseln in der maritimen Antarktis (James Ross Island, King George Island) auf ihre grundlegenden Bodeneigenschaften hin untersucht und ebenfalls anhand von Dichte und Korngröße fraktioniert, um die Verteilung des Bodenkohlenstoffs innerhalb der verschiedenen Fraktionen zu analysieren.

III. Der Zustand organischer Bodensubstanz in der sibirischen Arktis

Die dritte Studie zielte darauf ab, die Tiefenverteilung verschiedener Bodenfraktionen und deren chemische Zusammensetzung zu bestimmen, um die Speicherung von organischem Kohlenstoff in sehr organikreichen arktischen Böden besser zu verstehen. Bodenkerne von der Insel Samoilov im Lenadelta in der sibirischen Arktis wurden untersucht, um Informationen über die Tiefenverteilung von OM und dessen chemische Zusammensetzung zu erhalten. Die Gesamtbodenproben wurden separiert, um partikuläre (POM) und mineral-assoziierte OM-Fraktionen (MAOM) für weitere Analysen zu erhalten und deren chemische Zusammensetzung zu untersuchen.

In allen Teilen dieser Dissertation wurden OM-Fraktionen gemäß Dichte und Korngröße separiert und sowohl ihre Verteilung als auch ihre chemische Zusammensetzung untersucht. Die Böden der maritimen Antarktis (Studie I und II) wurden von grobkörnigen MAOM-Fraktionen dominiert und enthielten kaum POM. In beiden Studien untersuchte ich die horizontale Verteilung der organischen Bodensubstanz. Die terrestrischen, mit biologischen Bodenkrusten bedeckten Probenahmepunkte in Studie I enthielten mehr POM als das Seesediment und die regelmäßig überschwemmten Bereiche, was auf einen grundlegenden Aufbau von OM unter biologischen Bodenkrusten in einer störungsfreien Umgebung hinweist. Große POM-Fraktionen waren in den vegetationsfreien Böden aus Studie II signifikant weniger enthalten als in den Böden mit Vegetation. Hier zeigt sich der Einfluss der kargen Vegetation auf den Aufbau von OM in antarktischen Böden. Die chemische Zusammensetzung der entsprechenden POM-Fraktionen in Studie II ähnelte der Zusammensetzung des pflanzlichen Ausgangsmaterials, während sich die Tonfraktionen der vegetationsfreien Böden mit einem deutlich höheren Anteil an aromatischen Verbindungen von den Tonfraktionen der Böden mit Vegetation unterschieden. Die arktischen Böden in Studie III wiesen allgemein eine sehr heterogene Verteilung der OM-Fraktionen sowohl hinsichtlich der untersuchten Bohrkerne als auch hinsichtlich der Tiefe auf. Der Einfluss von Kryoturbation war ersichtlich durch tiefliegende, von POM dominierte Horizonte, die sich zwischen Horizonten befanden, die ihrerseits von MAOM dominiert wurden. Die chemische Komposition der großen POM-Fraktionen unterschied sich mit einem dominanten

Anteil an O/N-Alkyl-Verbindungen deutlich von der der Tonfraktionen mit größeren Anteilen an Carboxyl- und Alkylverbindungen, wobei sich die kleinen POM-Fraktionen als Übergangselemente zwischen großen POM- und MAOM-Fraktionen erwies.

In Studie I wurde gezeigt, dass die Entwicklung von biologischen Bodenkrusten und Böden in der unberührten Umgebung eines Süßwassersees auf James Ross Island, einer arid-polaren Insel in der maritimen Antarktis, eng miteinander verflochten sind. Mittels der Untersuchung eines Gradienten vom Seesediment hin zu terrestrischen, mit biologischen Bodenkrusten bedeckten Habitaten konnte gezeigt werden, dass sowohl die Entwicklung der biologischen Bodenkrusten als auch der Böden im Seesediment und in den regelmäßig überschwemmten Bereichen gestört und verzögert ist. Jedoch wurde gleichzeitig eine Zunahme an OM-Aufbau und Bodenentwicklung mit zunehmender Entfernung zum See beobachtet, die wiederum abbricht, nachdem Höchstwerte erreicht und überschritten wurden. Dieser Höhepunkt der Bodenentwicklung zeichnet sich durch die höchsten Kohlenstoff- und POM-Gehalte innerhalb des untersuchten Gradienten und signifikante Anpassungsmechanismen innerhalb der biologischen Bodenkruste, z. B. in Form von Membranverstärkung durch eine erhöhte Sitosterolproduktion, aus. Daraus schließe ich erstens, dass die Verfügbarkeit von Süßwasser in arid-polaren Gebieten entscheidend ist für die gemeinsame Entwicklung von Böden und biologischen Bodenkrusten, und zweitens, dass regelmäßige Störungen durch Überschwemmungen diese Entwicklung behindern.

Studie II zeigte, dass die spärliche Vegetation auf polaren Inseln in der maritimen Antarktis einen deutlichen Einfluss auf Verteilung der organischen Bodensubstanz und Bodenbildung hat. Ich habe Böden von James Ross Island und King George Island mit unterschiedlichen klimatischen Bedingungen und daraus resultierend unterschiedlich strukturierter Vegetation verglichen. Auf beiden Inseln wurden in Böden mit Vegetation mehr Kohlenstoff, Stickstoff und POM gefunden. Zudem enthielten die Tonfraktionen dieser Böden mehr tendenziell labile Verbindungen in den Tonfraktionen. Das polar-maritime Klima auf King George Island erlaubt das Wachstum vaskulärer Pflanzen, daher ist auf dieser Insel der unterirdische Eintrag von OM durch Wurzeln mit hoher Wahrscheinlichkeit für den ausgeprägteren Aufbau organischer Bodensubstanz entscheidend. Das Klima auf James Ross Island ist arid-polar und beschränkt die Vegetation auf Kryptogame, die in mattenähnlichen Strukturen wachsen. Daher liegt hier die Vermutung nahe, dass diese Strukturen als Retentionselemente wirken, die OM zurückhalten. In dieser Studie konnte gezeigt werden, dass die ungleichmäßige, lückenhafte Vegetation als

Hot Spot für biogeochemische Prozesse in diesen Böden dienen kann und dass Grasbüschel und biologische Bodenkrusten sowohl den Aufbau von OM als auch den Anteil an bioverfügbaren organischen Verbindungen fördern, die wiederum dazu in der Lage sind, mikrobielle Aktivität zu steigern.

Mit kohlenstoffreichen Bodenkernen von der Insel Samoilov in der sibirischen Arktis befasste sich Studie III. Das zentrale Ergebnis der Untersuchungen war, dass eben jene Fraktionen, die den Kohlenstoffspeicher dominieren, zugleich die labilsten sind. Alle POM-Fraktionen zusammen machen etwa 80 % des Kohlenstoffspeichers aus, wobei ca. 50 % allein in den großen freien POM-Fraktionen enthalten sind. Der organische Kohlenstoff in diesen POM-Fraktionen besteht aus eher labilen, leicht abbaubaren Verbindungen und wurde bisher durch die niedrigen Temperaturen konserviert. Anhaltende Erwärmung und weiteres Tauen werden sehr wahrscheinlich die Bioverfügbarkeit dieser Fraktionen erhöhen und damit ihren Abbau beschleunigen. Die gewonnenen Daten legen nahe, dass in diesem Szenario zukünftig sowohl kleine POM- als auch Tonfraktionen mit hoher Wahrscheinlichkeit den Kohlenstoffspeicher dominieren werden, da sie weniger leicht abbaubare Verbindungen enthalten.

In dieser Dissertation wurden sowohl Böden aus der Arktis als auch der Antarktis untersucht und dabei die Unterschiede zwischen den initialen Böden der maritimen Antarktis (Studie I und II) mit geringen Gehalten an OM und den Böden der sibirischen Arktis (Studie III) mit sehr fortgeschrittener Bodenentwicklung und großen Vorräten an OM aufgezeigt. Die Bodenentwicklung in der Antarktis befindet sich nach wie vor in einer initialen Phase, deren weitere Entwicklung unklar ist: Steigende Temperaturen könnten einerseits zu einer weiteren Ausbreitung der Vegetation führen und damit auch zu einer Beschleunigung von Bodenprozessen (vgl. Studie II), sollten andererseits die höheren Temperaturen jedoch mit einer sich intensivierenden Aridität einhergehen, könnten sowohl Vegetation als auch Böden in Zukunft noch mehr verarmen, da die Verfügbarkeit von Süßwasser ein Schlüsselkriterium für die Entwicklung von Böden und biologischen Bodenkrusten ist (vgl. Studie I). Kohlenstoffreiche arktische Böden, wie diejenigen, die in Studie III untersucht wurden, werden mit fortschreitender Erwärmung mit hoher Wahrscheinlichkeit Teile ihres Kohlenstoffspeichers verlieren. Diese Vermutung liegt darin begründet, dass ihre organische Bodensubstanz von Verbindungen dominiert wird, die sehr wahrscheinlich äußerst bioverfügbar sind, sobald die Konservierung durch Temperaturen unter dem Nullpunkt endet. Jedoch wird zusammen mit dieser Entwicklung voraussichtlich eine

Verschiebung des Kohlenstoffspeichers hin zu kleinen POM- und Tonfraktionen erfolgen, da im OM dieser Fraktionen stabilere Verbindungen vorherrschen.

Da sowohl Böden, Bodenorganismen als auch die Vegetation in der Arktis und der maritimen Antarktis in hohem Maße an die dort herrschenden widrigen Bedingungen angepasst sind, sind sie aufgrund der fortschreitenden Erwärmung mit grundlegenden Veränderungen konfrontiert. Daher werden mit dieser Arbeit wesentliche Informationen über den derzeitigen Zustand der untersuchten Böden und ihrer organischen Bodensubstanz zur Verfügung gestellt, die es ermöglichen, zukünftige Veränderungen durch Klimawandel und andere anthropogene Einflüsse zu verfolgen.

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Abbreviations

ASE	Accelerated Solvent Extraction
BSC	Biological Soil Crust
BSTFA	N,O-bis(trimethylsilyl)trifluoroacetamide
C	Carbon
C_{inorg}	Inorganic Carbon
C_{org}	Organic Carbon
CP-MAS	Cross-Polarization Magic Angle Spinning
C_t	Total Carbon
DCM	Dichloromethane
EC	Electric Conductivity
Fe_{Ox}	Oxalate-extractable iron oxides
Fe_D	Dithionite-extractable iron oxides
fPOM	Free Particulate Organic Matter
GC	Gas Chromatograph
IAEA	International Atomic Energy Agency
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IPA	International Permafrost Association
JRI	James Ross Island
KGI	King George Island
MAOM	Mineral-Associated Organic Matter
MeOH	Methanol
MS	Mass Spectrometer
N	Nitrogen
NMR	Nuclear Magnetic Resonance
NPP	Net Primary Production
OM	Organic Matter
oPOM	Occluded Particulate Organic Matter
oPOMs	Small occluded Particulate Organic Matter (<20 µm)
POM	Particulate Organic Matter
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
TMCS	Trimethylchlorosilane
V-PDB	Vienna Pee Dee Belemnite

List of publications and contributions

Peer-reviewed publications as first author

Study I – Initial soil development in maritime Antarctica

Prater, I., Heim, C., Angst, G., Rybalka, N., Mueller, C.W.
From water to land – mutual succession of microbial mats and soil at a freshwater lake in maritime Antarctica.
(In preparation to be submitted to Nature Ecology & Evolution)

Summary: Antarctica can be regarded as a perfect natural lab to study biogeochemical processes and interactions between biota and soil formation. As both cold and aridity hamper processes and as anthropogenic impact is low, plant-soil systems got preserved in a rather pristine state. So far, vascular plants find a habitat only on islands northwest of the Antarctic Peninsula, while cryptograms are common in ice-free areas. Precipitation is scarce in this region; therefore, the availability of freshwater is decisive for all life. Cryptogams form biological soil crusts (BSC) that often act as predecessors for higher plants under these rather hostile conditions representing an initial stage in terrestrial plant-soil co-evolution. When plants moved from water to land, some adaptation mechanisms (e.g. rigid cell walls, interaction with fungi) were necessary that are also decisive for survival under a polar climate regime. In this study, I provide insight in the interwoven development of initial soils concomitant to BSC in the vicinity of a freshwater lake on James Ross Island in the Weddell Sea and thus demonstrated the key role of hydrology in this co-evolution. I examined a gradient from the lake sediment of the freshwater lake towards terrestrial habitats covered with BSC in order to evaluate changes in the interaction of evolving vegetation and soil biogeochemistry.

The methods applied in my study include physical soil fractionation according to density and grain size, analysis of carbon (C) and nitrogen (N) contents of bulk soils and soil organic matter (SOM) fractions, extraction of dithionite- and oxalate-soluble iron oxide fractions and total digestion of bulk soil samples, extraction of lipid biomarkers from the bulk soils as well as stable isotope measurements ($\delta^{13}C$, $\delta^{15}N$) and ^{13}C CP-MAS NMR spectroscopy of particulate organic matter (POM) and clay-sized mineral-associated organic matter (MAOM) fractions. I examined a gradient

from the lake sediment of a freshwater lake towards terrestrial habitats covered with BSC. My results show that freshwater is crucial for both soil development and evolution of BSC, while both are closely linked and retarded by the harsh environment. I demonstrated that both soil development and development of adaptation mechanisms within the components of the BSC are most pronounced in the terrestrial habitats that are not disturbed by regular flooding – as long as freshwater is still available. With greater distance to the lake, a decline in accumulation of SOM and the extent of soil development could be observed. In addition, I was able to demonstrate that various communities of cryptogams and microorganisms determine the trajectory of the evolution of this vegetation-microorganism-soil system that would be outcompeted under less harsh environmental conditions.

Contribution: I fractionated the samples and performed elemental analysis, extraction of iron oxide fractions, and ^{13}C NMR spectroscopy. I conducted further chemical analyses with support of G. Angst and C. Heim. Together with my co-authors, I evaluated and discussed the data. I visualized the data and wrote the manuscript.

Study II – Vegetation and soil development in maritime Antarctica

Prater, I., Hrbáček, F., Braun, C., Vidal, A., Meier, L.A., Nývlt, D., Mueller, C.W. (2021). How vegetation patches drive soil development and organic matter formation on polar islands. Geoderma Regional, 27, e00429. https//doi.org/10.1016/j.geodrs.2021.e00429

Summary: Soil development in Antarctica has been dominated by physical processes for millennia, but with ongoing warming biochemical processes will probably gain influence. Vegetation on the Antarctic continent is usually patchy and restricted to ice-free areas mainly along the continent's margins including the Antarctic Peninsula. On King George Island west to the Antarctic Peninsula with a maritime-polar climate regime vascular plants grow besides the typical cryptogam vegetation, while the vegetation on James Ross Island east to the Antarctic Peninsula with a polar-arid climate regime is restricted to cryptogams. Soil development and SOM accrual are retarded under polar conditions, but the patchy vegetation can likely act as hot spot for biogeochemical processes in the soil. I showed that vegetation patches foster the buildup of organic matter (OM) and the presence of bioavailable organic compounds that are able to enhance microbial activity and thus soil development under ongoing warming. Yet, if increasing temperatures lead to an accelerating aridity, an enhanced deceleration of biochemical soil processes is also a justified scenario.

I examined soils with and without vegetation from both islands to understand the role of vegetation for soil development in this region. The methods I used included the physical fractionation of bulk soil samples according to density and grain size, analysis of C and N contents of bulk soils and SOM fractions by dry combustion, extraction of dithionite- and oxalate-soluble iron, aluminum, manganese, sulfur, and phosphate fractions from bulk soils, and ^{13}C CP-MAS NMR spectroscopy of POM and clay-sized MAOM fractions. I demonstrated significantly higher C and N contents in soils with vegetation and a higher proportion of POM in these soils compared to soils without vegetation. However, in all examined soils C storage was dominated by clay-sized MAOM. In addition, SOM from soils with vegetation contained more rather labile C compounds, while the SOM from soils without vegetation was dominated by more stable compounds.

Contribution: I conducted physical soil fractionation, chemical analyses, and ^{13}C NMR spectroscopy, evaluated and visualized the data and discussed them with my co-authors. I wrote the manuscript.

Study III – The state of SOM in the Siberian high Arctic

Prater, I., Zubrzycki, S., Buegger, F., Zoor-Füllgraff, L.-C., Angst, G., Dannenmann, M., Mueller, C.W. (2020). From fibrous plant residues to mineral-associated organic carbon – the fate of organic matter in Arctic permafrost soils. Biogeosciences, 17, 3367-3383.

https://doi.org/10.5194/bg-17-3367-2020

Summary: Arctic permafrost soils play a crucial role in the global C cycle as they store enormous amounts of OM. Hitherto, most research on permafrost-affected soils from the Arctic focused on the investigation of bulk soils and a lot of information is available on C storage and turnover. However, only little is known about the mechanisms that stabilize organic C in these soils besides the preservation by freezing. To gain such information it is vital to differentiate bulk soils into specific fractions which can be assigned to different stabilization mechanisms and ecological

functioning. Thus, to obtain information on these stabilization mechanisms, I fractionated soils from Samoylov Island in the Siberian Lena River delta according to density and particle size and received different SOM fractions of varying chemical compositions.

I investigated the obtained SOM fractions with regard to their elemental, isotopic, and chemical composition to get insight into the differences between highly fibrous POM and the MAOM fractions. The methods used included analysis of C and N content by dry combustion of all SOM fractions and bulk soils as well as stable isotope measurements ($\delta^{13}C$, $\delta^{15}N$) and ^{13}C CP-MAS NMR spectroscopy of POM and clay-sized MAOM fractions. My results show that the SOM in permafrost-affected soils from the northern hemisphere can be assumed to be highly vulnerable under ongoing warming: I demonstrated that with the large POM fractions the most labile and highly bioavailable SOM fractions contribute most (about 60 %) to the C stock and that the C in these fractions is most likely prone to decomposition once thawing sets in. About 40 % of the C is stored in more stable C compounds in small POM and clay-sized MAOM fractions that are less prone to mineralization. I suggest that the OM of these fractions with assumed low bioavailability will represent the major C stock in a warmer future. In addition, the analysis of N balances demonstrated the central role of biological N fixation as N source in these soils. Yet, as about one third of the N is stored in the large POM fractions that are rather labile, thawing of these soils will presumably lead to an increase in mineral N cycling and N losses.

Contribution: I conducted elemental analyses, ^{13}C NMR measurements, and additional work in the laboratory, was responsible for management, evaluation, and visualization of the data, and wrote the manuscript.

Peer-reviewed publications as co-author

Campos-Pereira H, Makselon J., Kleja D.B., **Prater I.**, Kögel-Knabner I., Ahrens L., Gustafsson J.P. (2022) Binding of per- and polyfluoroalkyl substances (PFASs) by organic soil materials with different structural composition – Charge- and concentration-dependent sorption behavior. Chemosphere https://doi.org/10.1016/j.chemosphere.2022.134167

Contribution: I conducted ^{13}C NMR analyses, supported the evaluation of the respective data, and commented on the manuscript before and during the review process.

Angst G., Pokorný J., Mueller C.W., **Prater I.**, Preusser S., Kandeler E., Meador T., Staková P., Hájek T., van Buiten G., Angst S. (2021) Soil texture affects the coupling of litter decomposition and soil organic matter formation. Soil Biology and Biochemistry https://doi.org/10.1016/j.soilbio.2021.108302

Contribution: I conducted ^{13}C NMR analyses and supported the evaluation of the data. I discussed the manuscript with all authors prior to submission.

Canessa R., van den Brink L., Saldaña A., Rios R.S., Hättenschwiler S., Mueller C.W., **Prater I.**, Tielbörger K., Bader M.Y. (2020) Relative effects of climate and litter traits on decomposition change with time, climate and trait variability. Journal of Ecology https://doi.org/10.1111/1365-2745.13516

Contribution: I conducted ^{13}C NMR analyses, helped to evaluate the respective data, and commented on the manuscript.

Joly F.-X., Coq S., Coulis M., David J.-F., Hättenschwiler S., Mueller C.W., **Prater I.**, Subke J.-A. (2020) Detritivore conversion of litter into faeces accelerates organic matter turnover. Communications Biology. https://doi.org/10.1038/s42003-020-01392-4

Contribution: I supported the conduction and evaluation of the ^{13}C NMR analyses and the respective data evaluation and commented on the manuscript.

Möckel S.C., Erlendsson E., **Prater I.**, Gísladóttir G. (2020): Tephra deposits and carbon dynamics in peatlands of a volcanic region – lessons from the Hekla 4 eruption. Land Degradation & Development https://doi.org/10.1002/ldr.3733

Contribution: I supported the evaluation of ^{13}C NMR data, revised the manuscript and commented on manuscript and suggestions from reviewers during the review process.

Angst G., Mueller C.W., **Prater I.**, Angst S., Frouz J., Jílková V., Peterse F., Nierop K.G.J. (2019): Earthworms act as biochemical reactors to convert labile plant compounds into stabilized soil microbial necromass. Communications Biology https://doi.org/10.1038/s42003-019-0684-z

Contribution: I supported the spectroscopic analyses and commented on the manuscript.

Meier L.A., Krauze P., **Prater I.**, Horn F., Schaefer C.E.G.R., Scholten T., Wagner D., Mueller C.W., Kühn P. (2019): Pedogenic and microbial interrelation in initial soils under semiarid climate on James Ross Island, Antarctic Peninsula region. Biogeosciences https://doi.org/10.5194/bg-16-2481-2019

Contribution: I conducted physical soil fractionation and some of the chemical analysis, discussed the results, and commented on the manuscript.

Prietzel J., **Prater I.**, Colocho Huarte L.C., Hrbáček F., Klysubun W., Mueller C.W. (2019): Site conditions and vegetation determine phosphorus and sulfur speciation in soils of Antarctica. Geochimica et Cosmochimica Acta https://doi.org/10.1016/j.gca.2018.12.001

Contribution: I contributed to the chemical analysis, discussed the results and revised the manuscript.

Hobley E. and **Prater I.** (2018): Estimating soil texture from vis-NIR spectra. European Journal of Soil Science
https://doi.org/10.1111/ejss.12733

Contribution: I conducted the vis-NIR scanning and discussed the results.

Mergelov N., Mueller C.W., **Prater I.**, Shorkunov I., Dolgikh A., Zazovskaya E., Shishkov V., Krupskaya V., Abrosimov K., Cherkinsky A., Goryachkin S. (2018): Alteration of rocks by endolithic organisms is one of the pathways for the beginning of soils on Earth, Scientific Reports
https://doi.org/10.1038/s41598-018-21682-6

Contribution: I conducted the ^{13}C NMR measurements and supported the evaluation of the data.

1 Introduction

1.1 Permafrost and soil development in cold regions

Permafrost covers globally an area of about 22 Million km^2, approximately 17 % of the exposed land surface, while its major part (more than 98 %) is present in the Northern Hemisphere (Gruber, 2012). The term permafrost refers to a physical state defined as "ground (soil or rock and included ice and organic material) that remains at or below 0 °C for at least two consecutive years" (Dobinski, 2011; von Everdingen, 1998). The International Permafrost Association (IPA) differentiates continuous, discontinuous, sporadic, and subsea permafrost as well as isolated patches that comprises both the Arctic and Antarctica and regions with mountainous permafrost (Brown et al., 2002).

The genetic factors of any soil development are parent material, climate, biota, relief, and time – an equation first phrased by Zakharov (1927) and later made popular by Jenny (1941). In cold regions, climate is the predominant factor besides the parent material as low temperatures hamper biological and chemical processes and thereby retard soil development (Tedrow et al., 1958). Permafrost itself has a significant impact on soil development. A typical process is cryoturbation, the regular thawing and freezing of the active layer, the layer above the permafrost table that deranges soil horizons (Munroe and Bockheim, 2001; von Everdingen, 1998). The regular freezing and thawing also facilitates physical processes like frost heaving and cryoclastic weathering (Munroe and Bockheim, 2001). Both polar regions share harsh and hostile conditions with short growing seasons caused by low temperatures and a lack of light during the polar night and large temperature differences between winter and summer. These lead to similar pedogenic processes that are differently pronounced in the subpolar and polar zone, e.g. organic matter (OM) accumulation, redoximorphism, or desert pavement formation (Goryachkin et al., 2004). Yet, climatic and geogenic differences between the Northern and Southern Hemisphere lead in general to fundamentally different statuses of soil development (Goryachkin et al., 2004).

In Antarctica, soil development is restricted to ice-free areas that are only present along its periphery, *e.g.* in the region of the Antarctic Peninsula, and in mountain ranges in the interior, like the Transantarctic Mountains (Bockheim et al., 2015) with a sharp transition to ice (Goryachkin et al., 2004). Burton-Johnson et al.

(2016) assessed 0.22 % of Antarctica to be ice- and snow-free, an area of 30,900 km^2. Despite the comparably small area, the variety of parent material originates various soil types (Bockheim et al., 2015). Due to the isolated location of the Antarctic continent, the vegetation is depauperate and mostly restricted to cryptogams with only two vascular plants native in maritime Antarctica, west of the Antarctic Peninsula: *Deschampsia antarctica* (Antarctic hair grass) and *Colobanthus quitensis* (Antarctic pearlwort) (Smith, 1993). Overall, the winters in Antarctica are warmer and the summers colder than in the Arctic, with decreasing temperatures and precipitation from the Subantarctic zone southwards to the continental cold desert (Goryachkin et al., 2004). Along this gradient, OM accumulation, podzolization, acidification, clay formation, and redoximorphism abate, while permafrost, salinization, alkalinization, and desert pavement formation become more important (Bockheim and Ugolini, 1990; Goryachkin et al., 2004).

In the Arctic, a similar shift along the gradient from the Subarctic zone northwards to the High Arctic with decreasing temperatures and precipitation can be observed, while precipitation also decreases from the coasts landwards. However, the land-to-sea ratio is much narrower in the Arctic compared to Antarctica, the vegetation is considerably richer, and the substrate has a finer texture and is more calcareous (Goryachkin et al., 2004). The presence of vegetation in combination with ice-rich permafrost that impedes drainage causes saturation zones that, together with very low temperatures, hamper the decomposition of plant litter, therefore OM accumulation is one of the dominating pedogenic processes in the Arctic (Munroe and Bockheim, 2001; Ovenden, 1990). Redoximorphism, podzolization, and to a lesser degree textural differentiation together with OM accumulation are the pedogenic processes that become less important along the northward gradient, while calcification, salinization, and desert pavement formation gain.

1.2 Carbon storage and cycling in permafrost-affected soils

Five interacting pools form the global carbon (C) cycle: Oceans represent the largest pool (approx. 39,000 Pg C); gas, oil, and coal reserves constitute the pool of fossil fuels (approx. 1,000 to 2,000 Pg C), the terrestrial pool (approx. 3,650 to 4,750 Pg C) that consists of soils on one hand and all biota – living and dead – on the other hand, and the atmosphere as smallest pool (approx. 860 Pg C) (Friedlingstein et al., 2020; Lal, 2010). In addition, there are pools like marine sediments and carbonate rocks that contain noteworthy amounts of C, but as these pools do not interact with other pools, the stored C is not in circulation (Lal, 2010).

Soils represent the largest active terrestrial C pool and therefore play a significant role in the global C cycle. The amount of C globally stored in soils down to a depth of 1 m was first estimated by Batjes (1996) to about 2,200 Pg C, of which 70 % were assessed to be organic C. Subsequent studies estimated for soils all over the world that between 1,408 Pg and 1,502 Pg soil organic C (SOC) are present within the first meter and between 1,993 Pg and 2,060 Pg SOC within the first two meters (Batjes, 2016; Jobbágy and Jackson, 2000). In addition, Jobbágy and Jackson (2000) estimated the global SOC content down to a depth of 3 m to be 2,344 Pg, highlighting that in a depth between 1 and 3 m soils contain about the same amount of C as is stored in the atmosphere.

Deep soil profiles with noteworthy C contents are more common in regions where permafrost and peatlands occur than in the temperate or tropical zone (Jackson et al., 2017). However, the depth of the soils is only one factor regarding the huge amount of C stored in permafrost-affected soils, especially in the Arctic. During the Quaternary, large amounts of soil organic matter (SOM) accrued in Arctic soils. During warmer periods, plant litter entered the soils and was conserved by processes that occur in colder periods like cryoturbation and the slowing down of mineralization of OM (Ping et al., 2015; Zubrzycki et al., 2014). First estimations on the SOC in permafrost-affected soils of the North were rather limited, because the available information was scarce and the authors often neglected specific processes and the depth of the soils, *e.g.* reckoned Post et al. (1982) that 191 Pg SOC are stored in Tundra soils covering an area of 8.8 million km^2.

With more data available, estimations became more comprehensive, *e.g.* showed Tarnocai et al. (2009) that permafrost-affected soils of the Northern Hemisphere encompass an area of approx. 18.8 million km^2 and that the respective soils contain 1,024 Pg SOC within the first three meters. The authors also added C pools from greater depth, namely yedoma sediments and deltaic deposits, that account for another 648 Pg for the depth below 3 m leading to a combined SOC content of 1,672 Pg SOC in the permafrost region (Tarnocai et al., 2009). Hugelius et al. (2014) provided a more detailed estimation on C stocks in the northern circumpolar region, thus 1,035 Pg SOC are stored in the first three meters of these soils, including 34 Pg SOC from poorly developed High Arctic soils. Below 3 m depth 91 Pg SOC are stored in deltaic alluvium and 181 Pg SOC in yedoma sediments, adding up to a total of 1,300 Pg, whereof about 800 Pg SOC are stored in the perennial frozen layers of permafrost-affected soils (Hugelius et al., 2014). Using advanced geospatial approaches that consider both horizontal and vertical heterogeneity in permafrost-affected soils, Mishra et al. (2021) provided an updated estimation that resulted in about 1,014 Pg SOC in the first 3 m of permafrost soils of the Northern Hemisphere, including approx. 14 Pg SOC from soils in the Tibetan permafrost region. The authors also showed that soils in mountainous permafrost regions store less C in deeper soil layers, while most C in permafrost-affected soils from the plain was stored in a depth between 1 and 2 m (Mishra et al., 2021).

It is no surprise that most estimations on C stocks in the permafrost region focus on the Arctic as more than 98 % of permafrost at the land surface are present in the Northern Hemisphere (Gruber, 2012). Of Antarctica, only an area of about 30,900 km^2 is ice-free and allows soils to develop (Burton-Johnson et al., 2016). Therefore, permafrost-affected soils in the Arctic contribute much more to the global C budget than soils of Antarctica.

In both the Arctic and Antarctica accumulation and turnover of SOM are primarily governed by climate – harsh conditions with short vegetation periods, cold temperatures and large temperature amplitudes determine the vegetation and therewith the net primary production (NPP). At the same time, biogeochemical processes in the soils are subject to climatic conditions, meaning that the turnover of SOM proceeds very slow as most processes are decelerated by cold temperatures. The Arctic and parts of Antarctica, namely maritime Antarctica, are counted among the fastest warming regions on Earth and therefore face profound alterations in many respects (Constable et al., 2021).

1.3 Permafrost-affected soils and climate change

"Climate change impacts and cascading impacts in polar regions, particularly the Arctic, are already occurring at a magnitude and pace unprecedented in recent history, and much faster than projected for other world regions. The polar regions, notably the Arctic and maritime Antarctic, are experiencing impacts from climate change at magnitudes and rates that are among the highest in the world, and will become profoundly different in the near-term future (by 2050) under all warming scenarios." (Constable et al., 2021)

This quote from the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) sums up the challenges that especially the Arctic and maritime Antarctica face. Warming trends in the region of the Antarctic Peninsula have already been observed about 30 years ago (King, 1994; Stark, 1994), including their impact on the vegetation (Smith, 1994). Moreover, the Antarctic Peninsula region is one of three regions that have been identified as areas of recent rapid regional warming indicating that mean annual air temperatures (MAAT) rose by more than 1.5 °C during the second half of the 20th century compared to a general warming of about 0.5 °C on average (Vaughan et al., 2003). During the last years, several temperature records have been observed in the Antarctic Peninsula region including a heatwave in February 2020 with temperatures up to 18.3 °C (González-Herrero et al., 2022; Turner et al., 2021).

The Arctic is warming more than twice as fast as all other regions in the world (Moon et al., 2021), and scientists recently presented their findings that it is in fact warming even four times as fast (Jacobs et al., 2021). The surface air temperature in the Arctic between October 2020 and September 2021 marked this period as the 7th warmest year on record, while this temperature was at least 1 °C above the long-term average for every year since 2014 (Moon et al., 2021). With 38 °C the highest documented temperature north of the Arctic Circle was measured during a heatwave in northeast Siberia in June 2020 (Overland and Wang, 2021).

Increasing temperatures lead to alterations in all parts of the Earth system and in the global C cycle: the extent of sea ice and continental ice sheets shrinks, marine and terrestrial ecosystems and food webs change, vegetation zonation shifts, and permafrost decreases while the active layer gains thickness (Fischer et al., 2018; French, 2007). Permafrost-affected soils in the Arctic acted as a C sink for millennia, but ongoing warming amplifies the likelihood that they turn into a C source when biochemical processes are no longer hampered by cold temperatures and waterlogging (Oechel et al., 1993). However, C losses from permafrost-affected soils might be tempered by the interplay of OM, mineral surfaces, microbial processes, and substrate quality (Gentsch et al., 2018; Tang and Riley, 2015).

In both polar regions, expanding vegetation may foster an enhanced CO_2 uptake, while amplifying aridity could also lead to a desiccation of the vegetation (greening vs. browning; Amesbury et al., 2017; Cannone et al., 2022; Moon et al., 2021; Parmentier et al., 2017; Robinson et al., 2018) with the respective impact on the abundance and quality of SOM. Higher temperatures and precipitation could also alter soil development by enhancing chemical weathering (Gislason et al., 2009; Norton et al., 2014). Adaptive shifts within the soil fauna have already been reported, while it is likely that Arctic and Antarctic communities respond differently to changing conditions (Andriuzzi et al., 2018; Nielsen and Wall, 2013). In the Arctic, permafrost thaw will presumably release large amounts of plant-available N with consequences for both the microbial and the plant community (Beermann et al., 2015; Keuper et al., 2012; Kicklighter et al., 2019). However, not only N may be released during permafrost thaw, but also other nutrients as well as methane and heavy metals that have been locked in the frozen ground (Knoblauch et al., 2018; Lawrence et al., 2015; Loiko et al., 2017; Reyes and Lougheed, 2015; Schuster et al., 2018).

Due to the complexity of the system, contradicting observations regarding the effects of climate warming on permafrost-affected soils have been made and comprehensive information about properties of SOM in permafrost-affected soils is still missing.

1.4 The role of soil organic matter fractions for the assessment of C sequestration

Soil organic matter represents a blend of heterogeneous constituents with different turnover times and is rather a continuum of organic substances representing the complete range from plant material to strongly altered organic compounds than a set of specific substances (Lehmann and Kleber, 2015; Wang and Hsieh, 2002). Therefore, the separation of different SOM fractions and their analysis offers a deeper insight into the chemical composition and other characteristics of the soil than the analysis of bulk soil samples alone and allows for the investigation of carbon pools that differ in structure and function (Christensen, 2001; Golchin et al., 1994; Six et al., 2002).

Under temperate climate conditions three mechanisms dominate the sequestration of SOC: protection by occlusion in aggregates, stabilization by association with mineral particles, and preservation by intrinsic recalcitrance of the organic substance (Lützow et al., 2006; Six et al., 2002). However, compared to temperate or warmer climate regimes, turnover times of SOM are clearly longer in cold regions (Carvalhais et al., 2014; Frank et al., 2012), because its mineralization is retarded by low temperatures and waterlogging, typical phenomena in polar regions (Oades, 1988). Especially in the Arctic, cryoturbation transports SOM into greater depth leading to an additional preservation of SOM in the permafrost (Kaiser et al., 2007).

Yet, permafrost thaw leads to a drop of these additional climate-driven sequestration mechanisms and to an accelerating mineralization of SOM (Plaza et al., 2019; Turetsky, 2004). If cold temperatures come along with sufficient water-availability, the growth of vegetation is less limited than microbial activity, what in consequence will lead to SOC accumulation (von Lützow and Kögel-Knabner, 2009; Wiesmeier et al., 2019). This is especially true in the Arctic, while in Antarctica NPP and C mineralization are both hampered by low temperatures and aridity. With rising temperatures, climatic stabilization decreases and is replaced by other sequestration mechanisms, e.g. inclusion in soil aggregates or binding to mineral surfaces (Harden et al., 2012; Mueller et al., 2015; Schmidt et al., 2011).

Therefore, the separation of specific SOM fractions and the investigation of their properties is an appropriate approach to support the identification of the respective sequestration mechanisms.

2 Objectives and hypotheses

The core of this thesis was to focus on the following aims and hypotheses and to answer the corresponding questions:

(1) I aimed at gaining deeper insights into the chemical composition of SOM in permafrost-affected soils and its horizontal and/or vertical distribution. My hypotheses include first, that Antarctic soils feature overall a coarser texture compared to Arctic soils, second, that particulate organic matter (POM) is scarce in Antarctic soils and that vegetation and freshwater availability are decisive for its buildup and distribution, and third, that the soils from the Siberian Arctic show signs of cryoturbation and contain large amounts of POM.

(2) Due to the harsh conditions in Antarctica, vegetation in general is limited, but biological soil crusts (BSC) are widespread in ice-free areas. My aim was to investigate the closely linked succession of BSC and elementary soil development following a gradient from a freshwater lake to terrestrial surroundings on a maritime Antarctic island. My main hypothesis here was that the availability of fresh water is crucial for both the succession of BSC and fundamental soil development processes, and that a development of adaption mechanisms within the constituents of the BSC can be observed along the gradient from the freshwater lake towards terrestrial habitats.

(3) Soil development in maritime Antarctica is mainly governed by physical processes, but with ongoing warming and the proliferation of vegetation, it is likely that biochemical processes gain in importance. I aimed at investigating the interplay of vegetation and soil development comparing soils with and without vegetation from two polar islands with differing climate conditions. Here, I followed two hypotheses: First, the spatial distribution of vegetation determines the distribution and composition of SOM under these climatic conditions. This is inscribed in the ratio between POM and MAOM. Second, the presence of vegetation has an immediate impact on the chemical composition of POM and MAOM fractions.

(4) In most permafrost-affected soils of the Northern Hemisphere tremendous amounts of organic carbon (OC) are stored. The aim in this study was to unravel the chemical composition of different SOM fractions and their distribution within the soil cores. I followed two main hypotheses while

investigating soil cores from the Siberian Arctic: First, particulate organic matter (POM) is dominating SOM in the respective soils as decomposition processes are restricted by cold temperatures. Second, as the degradation of OM is slowed down by the cold, the chemical composition of larger POM fractions reflects the chemical composition of the original plant litter, while smaller POM fractions and mineral-associated OM (MAOM) fractions are decoupled from the litter input.

3 Material and methods

3.1 Study areas, soil sampling, and sample preparation

The basis of this thesis form three studies from both the Northern and the Southern Hemisphere. In Study I and II, maritime Antarctica is in the center of interest, with Study I investigating samples from the vicinity of a freshwater lake on James Ross Island (JRI) east of the Antarctic Peninsula. For Study II, samples were taken from both JRI and King George Island (KGI) west of the Antarctic Peninsula. Study III focuses on the Siberian Arctic with samples taken from the Holocene River Terrace of Samoylov Island in the Lena River Delta. Table 1 gives an overview of the general locations:

Study area			Coordinates	
Study I – Initial soil development in maritime Antarctica				
James Ross Island, maritime Antarctica	Ulu Peninsula	White Lake	63°53'49.7''S	57°48'44.7''W
Study II – Vegetation and soil development in maritime Antarctica				
King George Island, maritime Antarctica	Fildes Peninsula	▪ Kristianka ▪ Drake Plateau ▪ 'Biologenbucht'	62°11'49.3''S 62°10'49.6''S 62°12'0.7''S	58°56'49.1''W 58°58'19.3''W 58°59'39.1''W
James Ross Island, maritime Antarctica	Ulu Peninsula	▪ Cap Lachman ▪ Berry Hill slopes	63°47'18.4''S 63°47'58.3''S	57°49'27.2''W 57°50'44.0''W
Study III – The state of SOM in the Siberian high Arctic				
Samoylov Island, Lena River Delta, Russian Arctic	Holocene river terrace		72°22'28.0''N	126°29'23.4''E

Table 1 Overview of the sampling locations of the three studies. From all individual sites, several samples were taken, so the coordinates refer to the general vicinity, on KGI, one transect was sampled on Drake Plateau, while two transects each were sampled at Kristianka and 'Biologenbucht'.

3.1.1 King George Island and James Ross Island, maritime Antarctica

The sampling for Study I was done on JRI, on a large ice-free area in the northwest of the island: Ulu Peninsula (63°56'S, 58°05'W). The climate on JRI is arid polar with a MAAT of about -7 °C and a mean annual precipitation estimated to 200 to 500 mm water equivalent (Engel et al., 2018; van Lipzig et al., 2004). However, characteristic are annual temperature variations of about 40 °C (-30 to +10 °C), persisting winds, and the predominance of snow that often drifts to the sea (Hrbáček and Uxa, 2020; Kavan et al., 2020). The parent material on JRI is primarily composed of Cretaceous marine sedimentary rocks and Neogene volcanic rocks (Francis et al., 2006; Smellie et al., 2008). Deglaciation is estimated to have started about 12,000 years ago (Oliva et al., 2017), the permafrost below the island is continuous with an active layer that reaches a thickness of between 50 and 90 cm (Bockheim et al., 2013; Hrbáček et al., 2017). On JRI, vegetation is restricted to cryptogams (Smith, 1993).

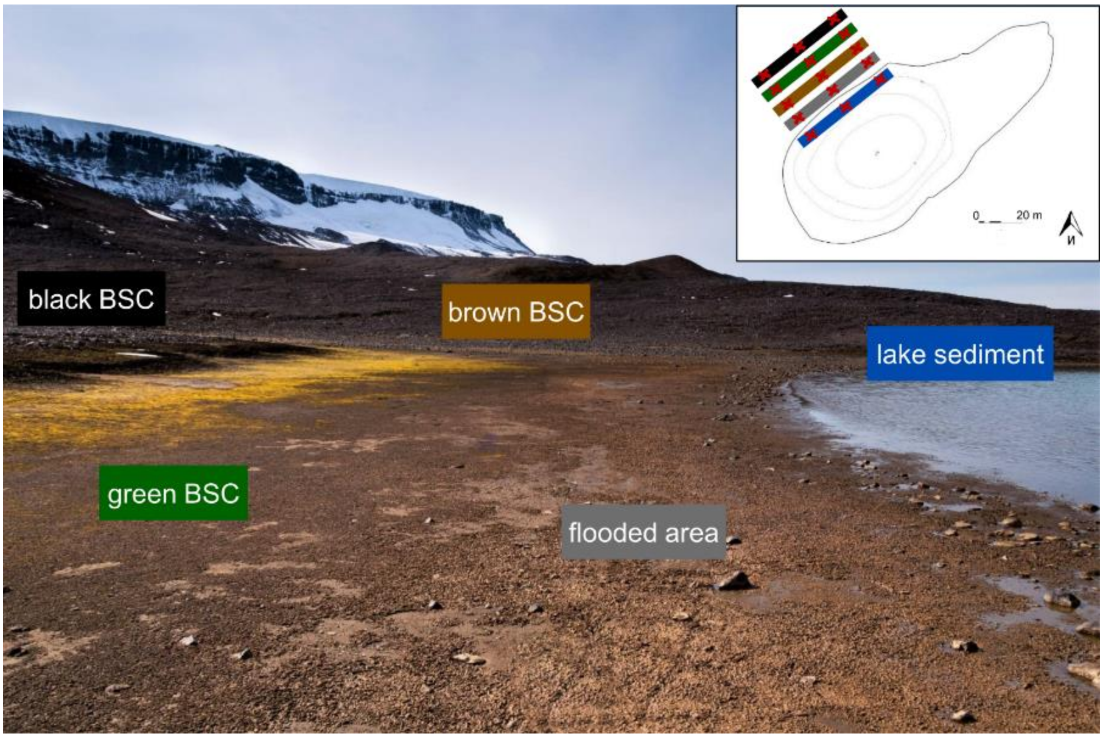

Figure 1 Sampling area Study III: Gradient from lake sediment of White Lake on James Ross Island towards terrestrial habitats covered by BSC. The small scheme of the lake in the upper right corner is taken from Nedbalová et al. (2013), red crosses indicate the sampling spots. Source: Prater et al. (2022).

For this sampling, the vicinity of White Lake was chosen, a freshwater lake in the eastern part of Ulu Peninsula. White Lake is a stable shallow lake with a mean depth of 0.7 m and an area of 6,662 m^2 (Nedbalová et al., 2013). During the respective sampling campaign in January and February 2016, three parallel gradients with five sampling spots each were sampled (see Figure 1) following the succession from the lake sediment to a regularly flooded area to terrestrial areas covered with brown, green, and black BSC. All samples were air-dried at a temperature of about 20 °C and subsequently sieved through a 2 mm mesh.

Study II involved the comparison of soils from two islands in the Antarctic Peninsula region in maritime Antarctica: JRI east of the Antarctic Peninsula in the Weddell Sea and KGI, part of the South Shetland Islands west of the Antarctic Peninsula. On both islands, large ice-free areas are present: Ulu Peninsula on JRI and Fildes Peninsula (62°12'S, 58°58'W) in the southwest of KGI (see Figure 2).

On KGI, the climate is polar maritime with a MAAT of about -2.5 °C and a mean annual precipitation of about 700 mm (Kejna et al., 2013; Michel et al., 2012) and thereby slightly warmer and more humid than on JRI Geology is dominated by Paleogene basalt-andesite lavas with sporadic outcrops (Smellie et al., 1984). Deglaciation set in about 10,000 years ago (Watcham et al., 2011) and below the peninsula, the transition from continuous to discontinuous permafrost passes with an active layer that is up to 180 cm thick (Bockheim et al., 2013). *Deschampsia antarctica* and *Colobanthus quitensis* are the only two native vascular plants that grow on KGI besides the typical cryptogam vegetation of the Antarctic Peninsula region (Komárková et al., 1985).

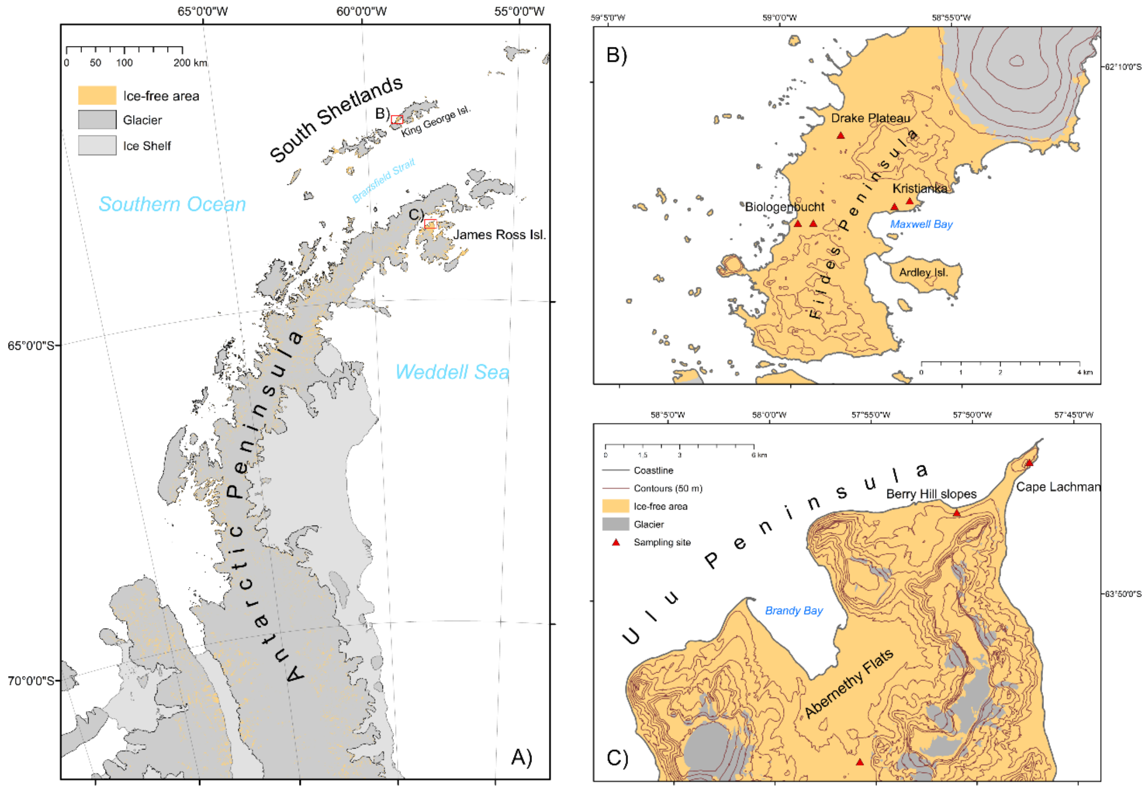

Figure 2 Sampling areas Study II: Panel A) shows the location of KGI and JRI west and east of the tip of the Antarctic Peninsula, panel B) shows Fildes Peninsula on KGI in detail with sampling spots (red triangles), and panel C) shows Ulu Peninsula on JRI in detail with sampling spots (red triangles). Source: Prater et al. (2021).

Soil sampling on KGI took place in February 2017 at five sites in three areas (see Table 1 for details). The uppermost 5 cm of soil along transects were sampled starting directly below *D. antarctica* patches towards vegetation-free areas at defined distances of 2.5, 5, 7.5, and 10 m, resulting in 25 soil samples on the whole from KGI. In addition, litter samples from the tussocks were taken. As the vegetation is differently distributed on JRI, another sampling pattern had to be applied. On JRI, the uppermost

5 cm of vegetation-covered soils (moss, lichen, and patchy moss) and bare ground were sampled in February 2017 and 2018, resulting in seven soil samples and additional litter material from living and dead moss. To improve comparability of the samples, I defined the samples from KGI with 10 m distance to the *D. antarctica* tussocks as vegetation-free for our detailed analysis of vegetation-covered and vegetation-free samples. Like the samples of Study I, all samples were air-dried at about 20 °C and sieved by 2 mm.

3.1.2 Samoylov Island, Russian Arctic

The samples of Study III were taken on Samoylov Island (72°22'N, 126°30'E) in the Lena River Delta in the Russian Arctic. The region's MAAT is -13.5 °C (1961-1990 Tiksi Hydrometeorological Observatory, Roshydromet (2019)) with large differences between warmest (July/August, 8 °C) and coldest (January, -32 °C) months. Islands in the river delta receive less precipitation compared to the mainland, with about 125 mm a^{-1} on Samoylov Island and about 323 mm a^{-1} in Tiksi at the shore, southwest of the river delta (Boike et al., 2013; Roshydromet, 2019).

Samoylov Island comprises a floodplain in the western part that covers about one third of its area and a Holocene river terrace in the eastern part where the samples were taken, as can be seen in Figure 3. Ice-wedge polygonal tundra with typical wet sedge tundra vegetation characterizes the Holocene river terrace (Boike et al., 2013; Zubrzycki et al., 2013). About 40 % of the polygonal tundra on the terrace are non-degraded, while the remaining 60 % are either completely collapsed or amid the degradation process (Kartoziia, 2019).

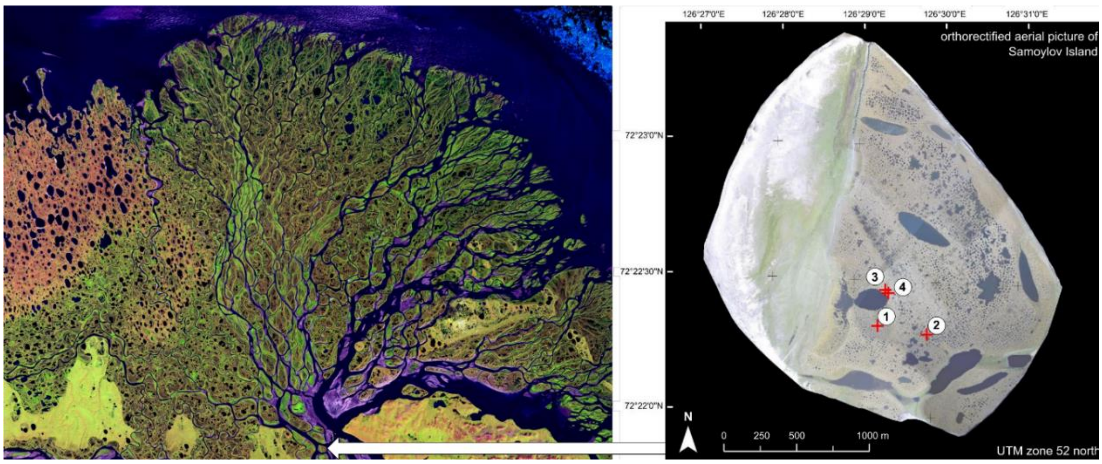

Figure 3 Sampling site Study III: On the left the Lena River Delta (Landsat 7 image, source: NASA (2021)), the white arrow indicates the location of the island within the delta; on the right a detailed aerial picture of Samoylov Island with sampling sites (red crosses) and numbers of the cores on the Holocene river terrace. Source: Prater et al. (2020), based on Boike et al. (2012)

Cryosols constitute the dominating soil group on the river terrace (FAO, 2014; Zubrzycki et al., 2013). During the sampling that took place in April 2011 and May 2013, four soil cores with a diameter of 76 mm and a length of about 1 m were drilled at the centers of ice-wedge polygons. Additional details on the sampling campaign are given in Zubrzycki (2013). The drill cores showed visually discernable soil horizons according to which the cores were separated when they were still frozen. After thawing, the samples were oven-dried at 40 °C. For our study, 23 depth increments were selected.

3.2 Analyses of bulk soil properties

3.2.1 Electric conductivity and pH (Study I, II)

To allow the analysis of both electric conductivity (EC) and pH in one step, deionized water was used. The measurements were conducted in a soil:solution ratio of 1:5 with a pH meter (WTW ph197i, Weilheim/Germany) combined with a glass electrode (Mettler Toledo InLab Expert DIN, Greifensee/Schweiz) and a portable conductivity meter (Mettler Toledo LE703, Greifensee/Schweiz).

3.2.2 Carbon and nitrogen content (Study I, II, III), differentiation between organic and inorganic carbon (Study I, II)

Bulk soil samples – and in Study II vegetation samples from vegetation-covered sites as well – were homogenized with a ball mill (Retsch, Haan/Germany) prior to the analysis. Milled sample material was weighed into tin capsules in duplicate and C and nitrogen (N) contents were measured by dry combustion at 1,100 and 1,000 °C, respectively (EuroVector EuroEA3000 Elemental Analyser, Pavia/Italy).

The soil samples of Study III were highly organic, therefore, I analyzed only total C (C_t). In this Study, I additionally calculated C and N stocks and projected them to a soil depth of 1 m.

For the bulk soil samples of Study I and II, the loss-on-ignition method was used to distinguish between organic (C_{org}) an inorganic C (C_{inorg}). Thereby, milled bulk soil samples were tempered at 550 °C for four hours in a muffle furnace (Carbolite ELF 11/6B, Neuhausen/Germany) to destroy C_{org} thermally (Hoogsteen et al., 2018). Afterwards, the tempered samples were analyzed for the remaining C content representing C_{inorg} by dry combustion. Subtracting C_{inorg} from C_t yielded the content of

C_{org}. For the samples of Study II, the contents of C_{inorg} were below the detection limit, therefore I reasoned that carbonates were not present to a noteworthy extent and equalized C_{org} with C_t.

3.2.3 Total digestion (Study I)

To determine the elemental composition of the parent material, I applied total digestion, an approach based on Jackson (1958) with adjustments by Lim and Jackson (1982): A mixture of perchloric acid ($HClO_4$) and nitric acid (HNO_3) was added to milled bulk soil samples to oxidize OM. After vaporizing the acid at a temperature of 300 °C, the samples were treated with hydrofluoric acid (HF). After a reaction time of >12 hours, $HClO_4$ was added. After the repeated vaporizing of the acid, the samples were treated with hydrochloric acid (HCl). The steps with HF and HCl were each performed twice. Subsequently, the samples were filtrated and the content of several elements were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista-Pro CCD Simultaneous ICP-OES, Palo Alto/USA). Three standard solutions were used: a sulfur (S) standard solution (Chem-Lab NV, Zedelgem/Belgium), a multi-element standard solution 14 elements (Al, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, Zn, K; Bernd Kraft GmbH, Duisburg/Germany), and a multi-element standard solution 9 elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si; Bernd Kraft GmbH, Duisburg/Germany). For our work, I selected Al, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, P, S, and Sr, as other elements were either not present or the contents were very low with huge deviations.

3.2.4 Oxalate- and dithionite extractable iron oxides (Study I, II)

The extraction of different iron oxide fractions is a common approach to derive information on soil development as it allows distinguishing between geogenic and pedogenic iron oxides (McKeague and Day, 1966). First, all iron oxides were extracted with a dithionite-citrate-bicarbonate solution at a slightly alkaline pH according to the method introduced by Mehra and Jackson (1960) based on the work of Mackenzie (1954). Second, the pedogenic iron oxides were extracted with an oxalate solution at a pH of 3 based on the work of Tamm (1922) adjusted by Schwertmann (1964).

The ratio of Fe_{Ox} and Fe_D is often applied as proxy for soil development, however, it has to be considered that the presence of magnetite is corrupting the extraction and can lead to an overestimation of iron values and prohibits the use of this ratio (Walker, 1983).

3.3 Physical soil fractionation (Study I, II, III)

I fractionated all bulk soil samples as described by Mueller and Koegel-Knabner (2009) with slight adjustments according to the respective sample material. The samples were density fractionated to receive POM fractions and grain size fractionated to receive MAOM fractions of different size.

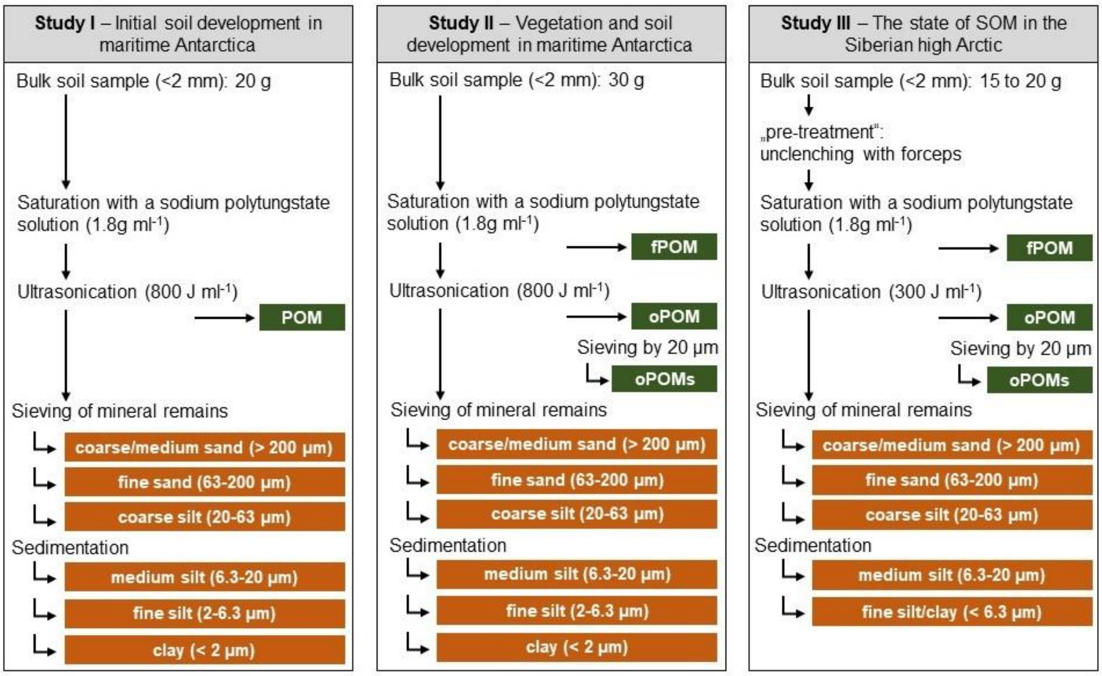

Figure 4 Combined density/grain-size fractionation schemes for the three studies with the yielded POM fractions (green) and MAOM fractions (brown) indicated.

Depending on how much sample material was available, 15 to 30 g of the bulk soils were saturated with a sodium polytungstate solution (TC-Tungsten Compounds, Grub am Forst/Germany) with a density set to 1.8 g cm^{-1}. After about 12 hours, the floating free POM (fPOM), the POM fraction not occluded in stable soil aggregates (Golchin et al., 1994) was separated by a vacuum system. Keeping the density, the samples were subjected to a calibrated energy by ultrasonication (Bandelin Sonoplus HD2200, Berlin/Germany). Subsequently, the floating occluded POM (oPOM), the OM particles embedded in water-stable aggregates (Golchin et al., 1994), was also separated by a vacuum system. Both fPOM and oPOM fractions were washed salt-free with deionized water, whereas the oPOM was sieved by 20 µm to obtain the small oPOM fraction (oPOMs) The mineral remains were also washed salt-free and subsequently sieved by 200 µm, 63 µm, and 20 µm to obtain coarse and medium sand, fine sand, and coarse silt, respectively. The mineral residue <20 µm was further separated using sedimentation, thereby the MAOM fractions medium silt, fine silt, and clay were obtained.

As the samples from the three studies showed very diverse compositions, some adjustments for single steps were necessary, these are illustrated in Figure 4:

3.4 Biomarker extraction (Study I)

The extraction of plant and microbial biomarkers was conducted on milled bulk soil samples by accelerated solvent extraction (ASE; Donex ASE 200, Dionex GmbH, Idstein/Germany) in Study I. Samples were weight into stainless steel cylinders with glass fiber filters at both ends. A mixture of dichloromethane (DCM) and methanol (MeOH) (9:1, v:v) at a pressure of $17x10^6$ Pa and a temperature of 75 °C with a heating and extraction time of 5 min each was used to extract solvent-extractable lipids (Angst et al., 2019; Jansen et al., 2006; Wiesenberg et al., 2004). Samples were extracted twice and subsequently dried using an N stream. The dried extracts were saponified with a 0.5 M KOH solution in MeOH:H_2O_{MilliQ} at a temperature of 80 °C for 2 hours. To separate the neutral fraction containing alcohols, alkanes, hopanes, ketones, and polar lipids from the acid fraction containing fatty acids, the solution was extracted five times with hexane.

The pH of the acid fractions was set to 1 using HCl before extracting it repeatedly (five to ten times) with DCM. Using column chromatography and sequential elution with hexane, DCM:hexane (2:1; v:v), and MeOH, the neutral fraction was separated into the three fractions: 1) aliphatics, ketones and hopanes, 2) alcohols, and 3) polar lipids.

Together with DCM/n-Hexane (1/2; v/v), alkane and ketone fractions were transferred into vials and the solvent were allowed to evaporate. To turn carboxylic groups into methyl esters, the fatty acid fraction was derivatized with trimethylchlorosilane (TMCS)/MeOH (1/9, v/v). To convert hydroxyl groups into trimethlsilyl ethers, the alcohol fraction was derivatized with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA).

Organic compounds were analyzed using a gas chromatograph (GC; Trace 1310, Thermo Fisher, Dreieich/Germany) coupled to a mass spectrometer (MS; TSQ Quantum Ultra Triple-Quadrupol-MS, Thermo Fisher, Dreieich/Germany). Full scan mode with a scan range of 50 to 600 amu was used to measure organic compounds that were identified on the basis of retention times and mass spectra of reference standards and published data.

3.5 Chemical analyses of soil organic matter fractions

3.5.1 Carbon and nitrogen content (Study I, II, III) and stocks (Study III)

Larger (>20 µm) SOM fractions were homogenized with a ball mill (Retsch, Haan/Germany) prior to the analysis, small (<20 µm) SOM fractions did not require any preparative treatment. Subsequently, the sample material was weighed into tin capsules in duplicate and C and N contents were measured by dry combustion as described in chapter *3.2.2* for bulk soil samples.

In Study III, I also calculated the C and N stocks for SOM fractions. Stocks were calculated for fPOM, oPOM, and oPOMs, while the different sand- and silt-sized MAOM fractions were combined to one fraction each for clarity reasons.

3.5.2 Abundance of stable isotopes ^{13}C and ^{15}N (Study I, III)

The abundance of the stable isotopes ^{13}C and ^{15}N for clay-sized MAOM and POM was analyzed using a combination of an isotope ratio mass spectrometer (Delta V Advantage, Thermo Fisher, Dreieich/Germany) connected with an elemental analyzer (EuroEA, Eurovector, Pavia/Italy). Acetanilide was used as lab standard that was calibrated against appropriate international isotope standards from the International Atomic Energy Agency (IAEA, Vienna/Austria). Results are given relative to air N_2 for ^{15}N and relative to Vienna Pee Dee Belemnite (V-PDB) for ^{13}C (Werner and Brand, 2001).

3.6 Chemical characterization of soil organic matter by ^{13}C CP-MAS NMR spectroscopy (Study I, II, III)

The chemical composition of selected SOM fractions (and plant litter for Study II) was investigated using ^{13}C cross-polarization magic-angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectroscopy (Bruker DSX 200 spectrometer, Billerica/USA). The following parameters were the same for all measurements: acquisition time of 0.01024 s, application of a ramped ^{1}H pulse (to circumvent Hartmann-Hahn mismatches), contact time of 1 ms. In addition, all samples were analyzed using 7 mm zirconium dioxide rotors at a frequency of 6,800 Hz.

According to the C content and the available amount of material of the respective samples, I adjusted other parameters. If enough sample material was available, the delay time for samples with a sufficient C content (plant litter, large POM fractions) was set to 1.0 s. For samples with lower C contents or samples with only small amounts of material available, the delay time was set to 0.4 s. I aligned the number of scans with the C content and the available sample material as well – samples with lower C contents and less material available needed more scans to achieve sufficient signal-to-noise ratios. In general, plant litter, fPOM, and oPOM samples needed between 3,000 and 20,000 scans, while oPOMs, POM, and MAOM samples needed up to 900,000 scans. Some spectra required line broadening to improve the signal-to-noise ratios in addition.

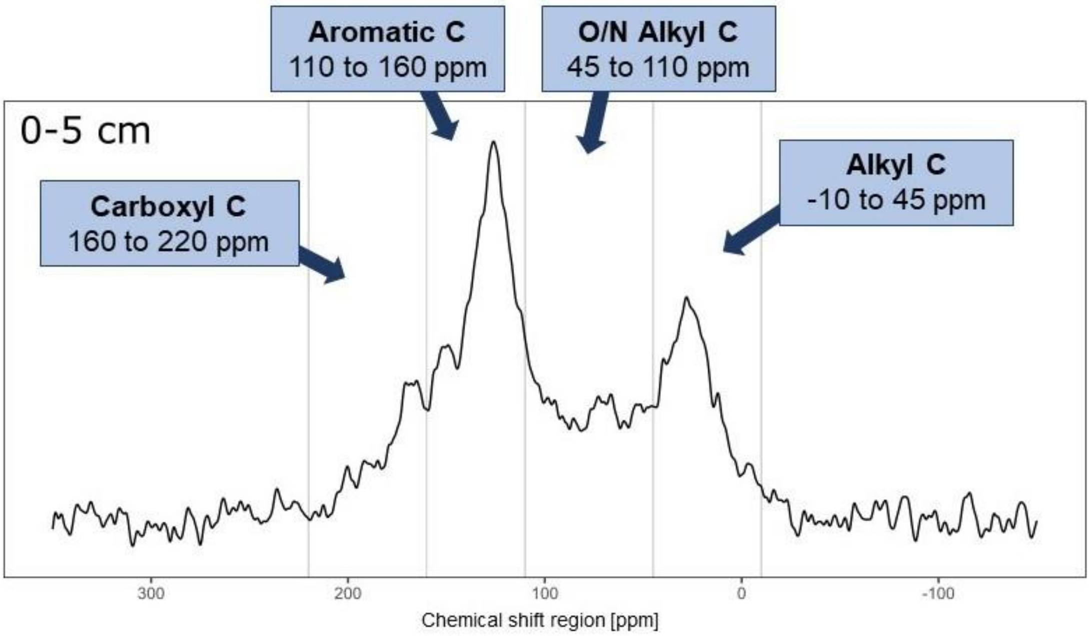

Figure 5 Exemplary ^{13}C CP-MAS NMR spectrum with an indication of the four chemical shift regions. Source: Supplementary material of Prater et al. (2021) with information on chemical shift regions added.

As the C content of the clay-sized MAOM fraction from Study III was very low, these samples were treated with HF to concentrate organic compounds by destroying mineral particles prior to NMR analyses (Gonçalves et al., 2003; Schmidt et al., 1997).

Tetramethylsilane was equalized with 0 ppm as reference for the chemical shift and spinning sidebands were included in the chemical shift regions if present. All spectra were integrated to receive the following four chemical shift regions: -10 to 45 ppm (alkyl C), 45 to 110 ppm (O/N alkyl C), 110 to 160 ppm (aromatic C), and 160 to 220 ppm (carboxyl C) (Beudert et al., 1989; Mueller and Koegel-Knabner, 2009; Wilson et al., 1981) as can be seen in Figure 5. I used the ratio of alkyl C to O/N alkyl C (a/o-a ratio) introduced by Baldock et al. (1997) and the ratio of the chemical shift regions 70 to 75 ppm and 52 to 57 ppm (70-75/52-57 ratio) introduced by Bonanomi et al. (2013) as proxies for the degree of decomposition of the SOM fractions. I also applied the molecular mixing model (MMM) by Baldock et al. (2004) and Nelson and Baldock (2005) that allows to transfer NMR spectra of OM into six compound classes (carbohydrate, carbonyl, char, lignin, lipid, protein).

4 Results and discussion

This section gives an overview about the central findings of the three studies performed for this thesis. Detailed information is available in the respective publications.

4.1 Distribution and chemical composition of different SOM fractions in permafrost-affected soils

I subjected the soil samples from all three studies to physical soil fractionation and separated different POM and MAOM fractions. Subsequently, the chemical composition of POM and clay-sized MAOM fractions were analyzed using ^{13}C NMR spectroscopy.

In Study I and II, the horizontal distribution of SOM fractions besides their overall distribution was analyzed. The soil samples of Study I were collected on JRI. Here, I analyzed a gradient from the sediment of a freshwater lake to terrestrial surroundings covered with BSC and aimed at understanding how SOM is distributed along this gradient. The soils from this study were dominated by the sand-sized MAOM fraction with a slightly higher proportion of fine material in the regularly flooded area (Prater et al., 2022). Due to the low content of OM, I separated only one POM fraction from these samples and found lowest contents in the lake sediment and highest in the site covered with green BSC.

The chemical composition of the clay-sized MAOM fractions was very similar along the gradient, but the POM fractions revealed differences with respect to their chemical composition. While two BSC-covered sites yielded very similar spectra with one dominating peak in the region of O/N alkyl C, the one that contained the most POM also showed a pronounced peak in the region of alkyl C. The POM fractions from the regularly flooded sites had a poor signal-to-noise ratio, but it was still identifiable that they contained clearly more aromatic compounds. The distribution of the POM fractions and their composition showed that lowest amounts of POM were present in the regularly flooded sites, while the amount first increased towards more terrestrial habitats, but declined again after the point of sufficient freshwater availability was overstepped (Prater et al., 2022).

I compared vegetation-covered and vegetation-free soils from two islands in maritime Antarctica with differing climate regimes in Study II. Soil physical fractionation revealed again a dominance of the sand-sized MAOM fraction and a very low abundance of POM in all examined soils. The vegetation-free soils from both islands contained the lowest amounts of POM, while the soils with vegetation showed large differences. Due to the different vegetation on both islands the sampling pattern had to be adjusted (*cf.* chapter 3.1.1). By far the highest amount of POM was found in a soil from JRI that was covered by dead moss. Overall, soils with vegetation contained significant more oPOM and fPOM than vegetation-free soils. While the vegetation-free soils contained hardly any large POM fractions, they yielded a low, but notable amount of oPOMs (Prater et al., 2021). This points either to the impact of horizontal transport by wind that is common in arid ecosystems (Throop and Belnap, 2019) or to the remains of former vegetation.

The NMR spectra of clay-sized MAOM fractions from vegetation-free soils from both islands revealed a high proportion of aromatic and alkyl C compounds despite a poor signal-to-noise ratio, while the clay-sized MAOM fractions from soils with vegetation contained more O/N alkyl and carboxyl C compounds. The spectra of all fPOM and oPOM fractions from JRI and KGI were dominated by O/N alkyl C compounds, similar to the spectra of the analyzed input plant litter. The oPOMs fractions from JRI showed an additional peak in the region of aromatic C. The a/o-a ratio as proxy for decomposition was lower in the large POM fractions than in the oPOMs fraction, indicating a less advanced decomposition for the large POM fractions (Baldock et al., 1997). This mirrors observations from temperate regions where POM occluded in soil aggregates turned out to be highly altered (Mueller and Koegel-Knabner, 2009).

In Study III, I investigated the overall distribution of SOM fractions and the vertical distribution within soil cores from Samoylov Island in the Siberian Arctic. The soil cores revealed a very high variability in their POM and MAOM contents (Prater et al., 2020). The impact of cryoturbation arose from deeper layers with high proportions of large POM fractions (fPOM and oPOM) that were located between MAOM-dominated depth layers. The small POM fraction (oPOMs) as well as the three analyzed MAOM fractions (clay-, silt-, and sand-sized) were likewise erratic distributed. Overall, no pattern within the depth distribution of the SOM fractions could be observed, underlining the influence of cryoturbation.

To allow assumptions on the potential decomposability of the SOM fractions, I combined the analysis of the chemical composition of SOM using ^{13}C NMR spectroscopy with the investigation of stable isotopes. Altering δ^{13}C values of OM in soils are subject to several factors, including the properties of the original input material, climate, and soil texture and are therefore not easy to interpret (Ågren et al., 1996; Nel et al., 2018). However, labile compounds like carbohydrates have in general higher values than more recalcitrant compounds like aromatics or lignin (Schmidt and Gleixner, 1997). The SOM fractions in Study III revealed only minor differences for the $\delta^{13}C$ values, but these values showed a high positive correlation with the decomposition proxies derived from ^{13}C NMR (a/o-a ratio, 70-75/52-57 ratio), indicating an initial decomposition stage of the large POM fractions. The NMR spectra of these large POM fractions were dominated by peaks around 70 ppm related to polysaccharides (Koelbl and Koegel-Knabner, 2004), while the spectra of oPOMs and clay-sized MAOM featured a dominant peak around 30 ppm related to aliphatic macromolecules like cutin or suberin (Koegel-Knabner, 2002). Overall, my analyses demonstrated pronounced differences between large POM fractions containing rather easily decomposable compounds and small oPOMs and clay-sized MAOM fractions consisting of compounds that are most properly less bioavailable (Prater et al., 2020).

4.2 Fresh water availability governs the intertwined development of biological soil crusts and soils in maritime Antarctica (Study I)

I investigated a gradient from the sediment of a freshwater lake on JRI to more terrestrial areas covered with BSC in Study I. The harsh climate on JRI restricts vegetation to cryptogams (*cf.* chapter 3.1.1), and as precipitation is scarce in the area, the availability of freshwater is decisive for biota. Along the gradient, I investigated bulk soil properties, SOM characteristics as well as the qualities of the BSC.

When cryptogams coalesce with soil particles, they form BSC, often following a succession starting with cyanobacteria, followed by green algae and later by lichens and bryophytes (Belnap et al., 2001a). Both soil, especially its depth and texture, and cryptogams influence the properties of the BSC (Belnap et al., 2001b). In addition, BSC act as trailblazer for higher plants by stabilizing the soil and providing nutrients (Yoshitake et al., 2010).

The ratio of Fe_{Ox} and Fe_D is often used as proxy for soil development as it refers to the ratio of pedogenic iron oxides (Fe_{Ox}) and the sum of both geogenic and pedogenic iron oxides (Fe_D) (McKeague and Day, 1966). Along the gradient, the ratio pointed to a very initial soil development in the lake sediment and a slightly more pronounced one in the terrestrial sites. The distribution of POM and C content was similar: very low in the lake sediment and slightly higher in the BSC-covered sites with highest proportions in the site with the green BSC (*cf.* Chaper 4.1; Prater et al., 2022).

The passage of green plants from freshwater to land required the development of several protection mechanisms for streptophyte algae that represent the point of origin for this evolutionary step (Becker and Marin, 2009; Dittami et al., 2017; Rensing, 2018). The development of rigid cell walls was just as essential as the establishment of defense mechanisms against abiotic stressors and as the evolution of an interrelation with fungi (Rensing, 2020, 2018). Some of these features are also pivotal for a life in hostile environments. Along the gradient, I found some evidence for these adaptions to harsh conditions. I found short-chained alcohols and fatty acids in the terrestrial sites and longer-chained compounds in the lake sediment indicating a warmer surrounding there, as short-chained compounds are typical protection mechanisms in cold and arid environments. In addition, C_{29} sterols where dominating in the two sites with the largest distance to the lake (green and black BSC), indicating an enhanced production of sitosterol, a membrane rigidifier typical for embryophytes. However, it has been demonstrated that algae modify their sterol content under cold stress to strengthen their membrane (Kumari et al., 2013).

Overall, the microbial community richness was rather small along the gradient with about 300 species with small portions of fungi, lichens, and bryophytes and a dominance of species that could not compete under less harsh conditions. Throughout the gradient unresolved complex mixture, partly decomposed nonpolar OM, was present indicating a slow decomposition that is typical as these harsh conditions with low temperatures and precipitation retard decomposition processes. Combining the results, I could show that soil development was most pronounced, while still on a low level, in the site covered with green BSC, the site where still enough freshwater was available from the lake, but no disturbances by flooding happened. Adaption mechanisms of the microorganisms where also most pronounced in this site, indicating the parallel development of soils and BSC and suggesting that freshwater availability is decisive in this hostile environment.

4.3 Vegetation determines SOM allocation and promotes soil development on islands in maritime Antarctica (Study II)

I investigated properties of bulk soils and SOM fractions from vegetation-free soils and vegetation-covered soils from two islands in maritime Antarctica in Study II. The separation of different SOM fractions revealed overall a very low proportion of POM and at the same time that vegetation-covered soils contained significant more large POM than vegetation-free soils (*cf.* chapter 4.1). In addition, the investigation of the chemical composition of the SOM fractions showed that the percentage of aromatic compounds was higher in clay-sized MAOM from vegetation-free soils, while the clay-sized MAOM from vegetation-covered soils contained more rather easy decomposable O/N alkyl C compounds. This means that the scarce vegetation fosters both the abundance of large POM fractions and augments the proportion of labile compounds within the SOM.

Yet, even with more POM present under vegetation, the C stock in all investigated soils is dominated by clay-sized MAOM as the proportions of POM are too low to have a notable impact on C storage. Regarding vascular plants, subsurface input of OM into soils plays an important role under temperate climate conditions (Rasse et al., 2005), but might be even more important in cold arid environments as bioturbation is lacking (Throop and Belnap, 2019). In hostile environments, plants tend to enhance their productivity by symbiosis with rhizobacteria and to have high root-to-shoot ratios while growing slowly, leading to relatively high belowground OM inputs (De Deyn et al., 2008). In addition, rhizodeposits that contain rather easily decomposable constituents contribute notably to OM input to soils and promote microbial activity and the accumulation of microbial necromass that is able to directly interact with mineral particles (Farrar et al., 2003; Kopittke et al., 2020; Rasse et al., 2005). Therefore, it seems likely that the input of OM by roots from the small *D. antarctica* patches plays a crucial role on KGI. On JRI, vegetation consists of mats of lichens or mosses that are larger by area than the tussocks on KGI. These mats act presumably as retention elements for the litter that is blown over the otherwise barren landscape, initiating OM accrual (Throop and Belnap, 2019).

While physical processes have been dominating soil development in Antarctica for millennia (Simas et al., 2015), the impact of vegetation on two islands in maritime Antarctica with vegetation determining both the presence of POM and the C pool in MAOM was demonstrated in this study (Prater et al., 2021). Further warming might lead to a proliferation of vegetation resulting in an even more pronounced influence of biological processes on soil development and in increasing amounts of POM, but with rising temperatures it is also possible that aridity is reinforced and maritime Antarctica becomes an even less habitable region for vegetation keeping soil development very slow (Prater et al., 2021).

4.4 Rather labile SOM fractions dominate the C stock in Arctic permafrost-affected soils (Study III)

The soil samples of Study III were very fibrous and especially the fibrous components, the fPOM fraction, contained the most C. This was also reflected in the C stock that was clearly dominated by the POM fractions that were responsible for about 80 % of the C stock with more of half of it stored in the fPOM fraction (Prater et al., 2020).

However, as illustrated above (*cf.* chapter 4.1) the large POM fractions that dominated the C stock in the investigated permafrost-affected soils rich in OM contain large amounts of labile C compounds, especially O/N alkyl C compounds, and are therefore presumably rather easily decomposable. At the same time, fPOM fractions are responsible for about one third of the N stock in these soils. Based on this data, I assume that it is very likely that the fPOM becomes more accessible for decomposers with ongoing warming and that large amounts of N are released during its mineralization, which could further accelerate the microbial mineralization of OM (Prater et al., 2020).

The thawing of these Arctic soils will have serious consequences for both C and N stock and cycling. It can be assumed that N bioavailability increases and that mineral N cycling will become more important (Altshuler et al., 2019; Voigt et al., 2017). The small POM fraction (oPOMs) consists of stronger decomposed organic particles that are closely connected to mineral surfaces (Wagai et al., 2009). I demonstrated for the first time for permafrost-affected soils that the oPOMs represents a coupling link between the large, rather labile POM and the MAOM that is rich in microbial-derived SOM.

The C stock in the permafrost-affected soils in my study is dominated by rather labile and presumably easily degradable SOM fractions. Therefore, I surmise that ongoing warming will lead to an enhanced decomposition of this large POM due to a higher bioavailability and a notable depletion of SOC. The degradation of this large POM will most likely not only lead to a release of C but also of noteworthy amounts of N what in turn could again accelerate microbial activity (Jilling et al., 2018). However, due to their chemical composition both oPOMs and clay-sized MAOM have the potential to act as more persistent C pools under warming conditions.

5 Conclusions

The aim of this thesis was to contribute to the deciphering of the impact of soil forming processes and vegetation on organic matter in permafrost-affected soils and with each of the three studies on which this thesis is based upon, I disclosed relevant information for the understanding of SOM in polar regions:

All three studies showed that the cold climate has a vast impact on SOM sequestration, buildup, and distribution as it slows down microbial processes, limits the habitat of both micro- and macroorganisms and of any vegetation, and helps to preserve SOM by freezing. The soils from maritime Antarctica (Study I and II) revealed a predominance of coarse fractions and low amounts of POM with the clay-sized MAOM dominating the C stock. In addition, the impact of vegetation and freshwater availability on soil development and SOM buildup in maritime Antarctica has been elucidated. The soils from the Siberian Arctic (Study III) contained large amounts of different POM fractions that were also dominating the C stock and showed clear signs of cryoturbation with deep buried horizons rich in SOM. All of these soils and their organic constituents are prone to alteration under persisting climate warming. However, the consequences are still not conceivable as contradictory effects have been observed.

In the pristine setting of an island in maritime Antarctica with a polar arid climate, I showed that the presence of freshwater is key for the development of both soils and BSC (Study I). Along a gradient from the sediment of a freshwater lake to terrestrial habitats covered with BSC, I could trace the intertwined evolution of the soils and the BSC that reach a peak when enough water is available, but no disturbance by flooding interferes with the development. In addition, evidence for adaption mechanisms towards cold and arid environments could be detected that adjusted along the gradient. For example, short-chained alcohols and fatty acids were found in terrestrial habitats, while longer-chained compounds were present in lacustrine sites that need less protection against cold and aridity. In terrestrial sites, a higher production of sitosterol, a membrane rigidifying substance, could also be observed compared to the lacustrine sites.

The dominating role of vegetation for the accrual of OM and its chemical composition on polar islands in maritime Antarctica was the second key finding in this thesis (Study II). Again, the cold climate is one of the decisive factors as it determines the presence and structure of vegetation on these islands. The slightly milder climate on KGI allows for the growth of vascular plants that grow in tussocks forming the typical patchy vegetation cover of drylands. Whereas the vegetation on JRI consists only of cryptogams that grow in mat-like structures. However, on both islands vegetation governs the presence of OM in the soils and its composition. I could show that the soils with vegetation contain clearly more C and large POM fractions than the soils without vegetation, and that the SOM in soils with vegetation contains more labile compounds. This means that in maritime Antarctica, where physical processes dominated soil development for millennia and soil properties strongly depended on the parent material, biological processes might gain influence under warming conditions. However, in this region – like in the Arctic – the interplay of several factors, *e.g.* precipitation, UV radiation, will determine if higher temperatures lead to a proliferation of vegetation and an increase in OM in the soils and an enhanced soil development or if intensifying aridity results in an amplified desiccation of the vegetation and OM-depleted soils.

For deep soils from the Siberian Arctic rich in OM that accrued for millennia, I demonstrated in Study III that the C stock is dominated by fractions that mainly consist of carbohydrates, *e.g.*, different saccharides and cellulose. For the preservation of the C in these fractions cold temperatures are decisive and thawing will presumably stimulate diverse processes. It can be assumed that during decomposition not all C will be lost, but parts will be converted into more stable compounds. In addition, as the respective fractions are also responsible for a notable proportion of the N stock, their decomposition will probably lead to an increase in N that will be available for both microorganism and plants. This could in turn lead to an enhanced plant growth, given that other factors like precipitation or aridity, respectively, do not hamper it. During this study, I also showed that the small oPOM fraction acts as a transitional C pool linking large POM fractions with MAOM – a phenomenon that was demonstrated for the first time in permafrost-affected soils. I also showed that, given their chemical composition with higher proportions of lipids and proteins and their C content, the small oPOM as well as the clay-sized MAOM have the potential to take over the key role for C storage as these SOM fractions seem to be less prone to mineralization even if the additional protection by freezing ends.

With this work, I could show the state of OM in permafrost-affected soils from both maritime Antarctica and the Siberian Arctic and could demonstrate how it is influenced by vegetation and soil forming processes. These permafrost-affected soils represent a very unique setting for the investigation of soil processes as they feature some characteristics that are hard to find anywhere else, *e.g.* a very low interference by human action, a very initial stage of soil development with low amounts of SOM in maritime Antarctica, and a very advanced stage of soil development with deep, OM-rich soils in the Siberian Arctic. Soils, soil biota, and vegetation in these regions are highly adapted to the harsh conditions under which they developed and are prone to fundamental changes if warming continues. Thus, it is important to have information on the current status of these soils and their SOM as provided by this thesis to enable the tracking of alterations caused by climate change and other anthropogenic interference in the future.

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Appendix

Appendix A - Studies

Study I - Initial soil development in maritime Antarctica

Prater, I., Heim, C., Angst, G., Rybalka, N., Mueller, C.W.

From water to land – mutual succession of microbial mats and soil at a freshwater lake in maritime Antarctica.

(In preparation to be submitted to Nature Ecology & Evolution)

Study II – Vegetation and soil development in maritime Antarctica

Prater, I., Hrbáček, F., Braun, C., Vidal, A., Meier, L.A., Nývlt, D., Mueller, C.W. (2021). How vegetation patches drive soil development and organic matter formation on polar islands. Geoderma Regional, 27, e00429. https//doi.org/10.1016/j.geodrs.2021.e00429

Study III – The state of SOM in the Siberian high Arctic

Prater, I., Zubrzycki, S., Buegger, F., Zoor-Füllgraff, L.-C., Angst, G., Dannenmann, M., Mueller, C.W. (2020). From fibrous plant residues to mineral-associated organic carbon – the fate of organic matter in Arctic permafrost soils. Biogeosciences, 17, 3367-3383.

https://doi.org/10.5194/bg-17-3367-2020

Appendix B – Publication Record

Publications in peer-reviewed journals as first author

Prater, I., Hrbáček, F., Braun, C., Vidal, A., Meier, L.A., Nývlt, D., Mueller, C.W. (2021). How vegetation patches drive soil development and organic matter formation on polar islands. Geoderma Regional, 27, e00429
https://doi.org/10.1016/j.geodrs.2021.e00429

Prater, I., Zubrzycki, S., Buegger, F., Zoor-Füllgraff, L.-C., Angst, G., Dannenmann, M., Mueller, C.W. (2020). From fibrous plant residues to mineral-associated organic carbon – the fate of organic matter in Arctic permafrost soils. Biogeosciences, 17, 3367-3383
https://doi.org/10.5194/bg-17-3367-2020

Publications in peer-reviewed journals as co-author

Campos-Pereira H, Makselon J., Kleja D.B., **Prater I.**, Kögel-Knabner I., Ahrens L., Gustafsson J.P. (2022) Binding of per- and polyfluoroalkyl substances (PFASs) by organic soil materials with different structural composition – Charge- and concentration-dependent sorption behavior. Chemosphere
https://doi.org/10.1016/j.chemosphere.2022.134167

Angst G., Pokorný J., Mueller C.W., **Prater I.**, Preusser S., Kandeler E., Meador T., Staková P., Hájek T., van Buiten G., Angst S. (2021) Soil texture affects the coupling of litter decomposition and soil organic matter formation. Soil Biology and Biochemistry
https://doi.org/10.1016/j.soilbio.2021.108302

Canessa R., van den Brink L., Saldaña A., Rios R.S., Hättenschwiler S., Mueller C.W., **Prater I.**, Tielbörger K., Bader M.Y. (2020) Relative effects of climate and litter traits on decomposition change with time, climate and trait variability. Journal of Ecology
https://doi.org/10.1111/1365-2745.13516

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