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An investigation into the potential of glacial flour as a novel soil treatment for crops

Sarah Tingey

A thesis submitted to the University of Bristol in accordance with the requirements for award of the degree of Doctor of Philosophy in the Faculty of Science

School of Geographical Sciences

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Abstract

There is an urgent need to address future global food production, enhancing crop yields to meet demands whilst ensuring nutritional value. However, increasing agricultural sustainability and resilience has become challenging due to climate warming. One potential method of improving soil fertility is the use of crushed rock, however this practice is limited by production costs. Glaciers act as natural 'sediment factories' known to finely crush underlying bedrock to fine particulates that are exported downstream in annual meltwaters. Only recently has the potential of glacial flour as an alternative to crushed rock for farming been considered a possibility. A global overview of glacial flour nutrient and trace element content from eleven geologically different glaciers was evaluated, highlighting the geochemical composition with the greatest agricultural potential. Two contrasting glacial flours, Chhota Shigri, Northwest Hindu Kush Himalaya (mixed bedrock granitic-gneiss with minor sedimentary bands) and Sólheimajökull glacier, Southwest Iceland (igneous mafic volcanic basalts) were investigated as potential soil fertility treatments for leguminous crops, soybeans (*Glycine max.* var Black jet). Himalaya and Icelandic glacial flour increased crop yields 85 % and 135 % above the control, whilst improved plant health, legume N-fixation capacity and nutritional value. Nutritional value of the soybeans is determined by trace element availability, which in turn is driven by the underlying geology beneath the glacier. Glacial flour enriched soybeans in beneficial dietary nutrients (calcium, iron and zinc) which suggests potential application as a micronutrient treatment to target soil micronutrient depletion. However, it is also demonstrated that glacial flours which contain toxic trace elements, such as Chhota Shigri flour containing arsenic, can result in toxic bioaccumulation in crops. Overall, the results indicate that glacial flour has potential to act as a novel soil treatment and micronutrient fertiliser but requires geochemically screening to avoid toxic elements.

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Covid-19 statement

This thesis was conducted during the global Covid-19 pandemic. The pandemic impacted this body of research. Over the course of the pandemic there was a lack of access to research laboratory facilities. Trace element analysis on the sediment and soybean was in some cases delayed in total by ten months from March 2020. However, when access was allowed, the methods for trace element extraction were not allowed to be performed at University of Bristol under the Covid lab safety rules (concentrated acid work was limited). The analysis work was then conducted at Newcastle University, after the winter 2020 lockdown they were able to run the total trace element extractions however I was not able to attend. The pandemic curtailed training and access to the ICP-MS facilities. Furthermore, I was unable to conduct method development surrounding a labile metal extraction because of limited access to facilities and safety rulings in place. This information would have provided novel knowledge surrounding bioavailability of glacial flour and as such there is a potential weakness in this area within my thesis.

Author's declaration

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's *Regulations and Code of Practice for Research Degree Programmes* and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

Signed: S. L. Tingey Date: 24/05/2022

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Chapter 1.
Introduction and Scientific Background

1.1 Introduction

Future changing climate is expected to cause severe, wide-ranging impacts upon food security (IPCC 2018a). Rising concentrations of atmospheric carbon dioxide (CO_2) and other greenhouse gases (CH_4, NO_x) will lead to global average surface temperatures increases (up to 5.4 °C by 2100 (IPCC 2022) and uncertain precipitation patterns, thus disrupting current agriculture (IPCC 2014). Precarious food production coupled with increasing world population growth is amplifying food insecurity, especially upon the most vulnerable in the Global South (Foley et al. 2011). Adapting food production methods to be more resilient and sustainable, particularly for poor communities, has the potential to moderate the most severe impacts (Foley et al. 2011; Altieri et al. 2015).

In addition to strengthening agricultural resilience, there is an urgent need to overcome malnutrition as a result of poor dietary intake (Micha et al. 2020). Diet related malnutrition is responsible for more than one-third of deaths in children under 5 worldwide and has been shown to hinder cognitive growth and economic potential, acting as a poverty trap for those afflicted, termed 'hidden hunger' (Gödecke, Stein, and Qaim 2018; Kennedy, Nantel, and Shetty 2003; WHO 2018). The 2030 UN Sustainable Development Goals (SDGs) hope to *'end hunger, achieve food security, improve nutrition and promote sustainable agriculture'* by supporting interventions addressing resilience and malnutrition (Nations 2015). Despite gains over the last decade, realising 2030 SDGs seems in doubt as the full impacts of the COVID-19 pandemic begin to unfold (Laborde et al. 2020; Béné 2020). Driven by a new sense of urgency, research and development of sustainable agricultural solutions is warranted.

Impelled by increasing pressure on food production systems, past research has generated a myriad of effective solutions; from the early 'green revolution' intensive agricultural strategies of the 1960's to current strategies such as nano-fertilisers, genetically modified crops, improving photosynthetic potential, radiation use efficiency and canopy architecture (Parry et al. 2011; Cole et al. 2018; Rebetzke et al. 2013; Prosekov and Ivanova 2018). However, without significant economic assistance, these high-tech interventions remain out of reach to resource constrained smallholder farmers. Low-input, poor smallholder farmers are essential food producers, responsible for > 50 % of the global food supply (Cole et al. 2018). There is a need for an alternative model that involves a more sustainable, socially just approach, whilst working within the current framework of smallholder food production. ‘Agroecology’, encompasses a variety of ecologically sensitive, sustainable agricultural styles adopted by approximately 75 % of the 1.5 billion smallholders, family farmers and indigenous people worldwide (Altieri and Nicholls 2012). Despite significant research gains of conventional agriculture since the 1960’s, agroecological processes and methods are poorly understood and have been largely ignored by the scientific community. Driven by a need for sustainable agriculture, there is now a paradigm shift towards optimising agroecological methods through scientific research (DeLonge, Miles, and Carlisle 2016).

One potential method that may enhance agroecological methods is the application of crushed rock to soils (Manning 2010). Over the last 30 years, research into crushed rock farming has been revived, driven by two potential uses; i) a low-cost soil treatment for farmers of the developing world, and ii) a potential CO_2 reduction strategy, termed ‘enhanced weathering’ (Beerling et al. 2018a; Kantola et al. 2017; Schuiling and Krijgsman 2006). Recent research has shown that the addition of crushed rock improves soil fertility indicators; enhancing nutrient and organic matter content, water holding potential and soil pH (Manning 2010; ten Berge et al. 2012; Liu and Lal 2014). The cumulative effect of improved soil fertility results in a propensity for greater crop yields, particularly for tropical / sub-tropical agriculture (Bakken et al. 2000; Beerling et al. 2018b; Mohammed et al. 2014; Priyono and Gilkes 2008b; Manning 2010; Theodoro and Leonardos 2006). Determinants for propitious crop yields have been shown to be particle size and geology (mineralogy and lithology, subsequent nutrient content, weathering potential) (Cronan 1985; Priyono and Gilkes 2008b). Past research into crushed rock farming within a low budget agroecological framework has focused on repurposing rock dust, prioritising particle size over geological composition (Priyono and Gilkes 2008b). The importance of geological provenance is highlighted following crop growth experiments that applied quarry and mine waste rock dust and achieved little effect on soil fertility and consequently poor crop yields (Bakken et al. 2000; Hartmann, West, Renforth, Kohler, et al. 2013). This indicates that there is a need for crushed rock possessing the desired physical and geochemical attributes whilst being low-cost and attainable.

One possible source of finely crushed rock is glaciers. It is well documented that glaciers are responsible for many physical landscape features, forming vast mountain ranges and distinctive valleys, acting as powerful agents of erosion (Cowton et al. 2012; Brown, Tranter, and Sharp 1996b). As such, glaciers create significant quantities of relatively unweathered sediment, 'glacial flour', that is delivered downstream into rivers and oceans, playing an active role in global biogeochemical cycles (Hawkings et al. 2016; Hawkings et al. 2015b; Hawkings et al. 2014; Lawson et al. 2014). One current study has investigated glaciolaucustrine Greenlandic glacial sediments (collected from the bottom of a proglacial lake), as a method to enhance crop yields, however there was little increase in crop growth compared to the control, the authors suggest this was due to limited chemical weathering of the sediments likely due to external factors (temperature, water availability), plant nutrients demands (such as Nitrogen (N)) and the low potential of geochemical weathering of Greenlandic granite compared to other bedrock types (Sukstorf, Bennike, and Elberling 2020).

Glacial flour plays an important biogeochemical role within glacial systems and has been shown to be relatively unweathered, highly geochemically reactive and containing many biologically important nutrients (N, Phosphorous (P), Silicon (Si), Iron (Fe), Mercury (Hg)) (Hawkings et al. 2016; Hawkings, Skidmore, Wadham, Priscu, Morton, Hatton, Gardner, Kohler, Stibal, and Bagshaw 2020; Hawkings et al. 2017; Hawkings et al. 2015a; Wadham et al. 2016; Hawkings et al. 2021). Knowledge of glacial sediments and biogeochemical processes has advanced considerably, however, studies have historically focused on small valley glaciers in the Arctic and Alps or large ice sheet catchments in Greenland and Antarctica (Delaney et al. 2018; Föllmi et al. 2009; Mitchell, Brown, and Fuge 2001; Tranter 2006; Hawkings et al. 2016; Hawkings, Skidmore, Wadham, Priscu, Morton, Hatton, Gardner, Kohler, Stibal, and Bagshaw 2020; Hawkings et al. 2017; Hawkings et al. 2015a). An equivalent understanding of nutrient export from glaciers outside of these regions, such as the Himalayas, has been slow to develop (Singh et al. 2003; Singh, Ramanathan, and Pottakkal 2016b). There is little information on sediment bound nutrients and potential fluxes to downstream environments. Consequently, Himalayan glacial flour may be more important to downstream ecosystems than originally thought (Wagnon et al. 2007; Wulf, Bookhagen, and Scherler 2010). Furthermore, by building upon current knowledge, it will enable an assessment of the potential for Himalayan flour as a supply source for sub-tropical / tropical agroecology.

The following scientific background looks to provide an overview of the current understanding of glacial flour for agriculture. The issue of food security and the need for new agricultural solutions is not new, however the development and enhancement of agroecological practices is a growing field of research. A background of the history of crushed rock agriculture, supported by an analysis of past crushed rock literature and research gaps is given. Sustainable sources of naturally crushed rock are assessed, and the current understanding of glacial flour biogeochemistry is discussed. The chapter finishes by identifying research gaps and the pathway this thesis will follow to further knowledge.

1.2 Scientific Background

1.2.1 Global agriculture

World population is rapidly growing, placing increasing demands upon our food production systems (Foley, Ramankutty, Brauman, Cassidy, Gerber, Johnston, Mueller, O'Connell, et al. 2011). The largest population growth will be seen within the 48 least developed countries, increasing from 954 million inhabitants in 2015 to 1.9 billion in 2050 and then further to 3.2 billion in 2100 (UNDSEA 2015). By the year 2050 we will need to produce up to 110 % more food (Tillman et al. 2011). On top of population growth, developing countries will become more affluent, switching their diet to one containing richer produce with more meat, thus increasing demand on agricultural systems further (Pradhan et al. 2013). Against this backdrop, changing climate is affecting our ability to grow crops, increasing uncertainties surrounding food security (IPCC 2018a, 2014, 2022). There are two potential agricultural solutions proposed to meet future food demands: agricultural expansion; and agricultural intensification (Nations 2015).

Agricultural expansion involves increasing available cropland by converting current uncultivated land (Tauger 2013; Stevenson et al. 2013). It has been shown that agriculturally-driven land clearing has removed 70 % of grasslands, 50 % of savanna, 45 % of the temperate deciduous forest and 27 % of the tropical forest, imperilling associated species biodiversity and ecosystem function (Foley, Ramankutty, Brauman, Cassidy, Gerber, Johnston, Mueller, O'Connell, et al. 2011; Tilman et al. 2017). Additionally, forest clearance is a major source of greenhouse gas emissions, estimated to release $1.1\text{x}10^{15}$ g of C per year, approximately 12 % of total global anthropogenic CO_2 emissions (Friedlingstein et al. 2010). From these considerable effects, it can be concluded that expanding agricultural land is not in line with the future of sustainable farming (Nations 2015).

Another proposal is that of agricultural intensification, in which existing lands are heavily managed to be more productive (Foley, Ramankutty, Brauman, Cassidy, Gerber, Johnston, Mueller, O'Connell, et al. 2011). Current intensive land management strategies originate from an urgent need to alleviate the food crises of the 1940s – 80s, their success is estimated to have saved up to 1 billion people globally (Stevenson et al. 2013). Following their development, uptake of 'Green Revolution' methods has continued, increasing global crop yields by 21 % from 1985 – 2005 (Foley et al. 2011). This effective approach involves a series of research, development and technology transfer initiatives, combining genetically modified high-yield variety crops, intense irrigation schemes, chemical fertilisers and pesticides (Evenson and Gollin 2003). However, despite these strategies achieving significant accomplishments, their continued adoption is unsustainable (Pingali 2012). One of the most controversial Green Revolution methods is the application of chemical fertilisers.

Global chemical fertiliser use has increased since 1985 by 500 % (P and K) and over 800 % (N) due to an urgent continuous need to provide enough nutrients to sustain crop growth and meet population food demands (Matson et al. 1997; Rostanski et al. 2016). Although soils can degrade naturally, it has been shown that the use of chemical fertilisers has exacerbated soil infertility; polluting soils, deteriorating soil structure, decreasing soil pH and disrupting soil microbial and invertebrate soil ecosystems (Savci 2012). Attempts to remediate soil infertility through additional chemical fertiliser applications impairs soil fertility further, generating a negative feedback loop and enhancing farmers reliance upon chemical fertilisers (Stevenson et al. 2013). As a result, there is now a direct need to rejuvenate soil fertility and improve crop yields without employing Green Revolution strategies.

1.2.1.1 Soil fertility – the problem with current agricultural practices

The FAO defines soil fertility as *'the capacity to receive, store and transmit energy to support plant growth… its available nutrient status and its ability to provide nutrients out of its own reserves'*- (Food and Agriculture Organization 2015).

Modern intensive farming methods have degraded soils, resulting in most global soil resources being of poor quality (Stevenson et al. 2013; ITPS. 2015). The application of soluble chemical NPK fertilisers has been determined as a key cause of soil degradation (Montgomery 2007). There are four issues associated with the use of chemical fertilisers that occur across various stages of the chemical fertiliser cycle (from production costs to point of use) and span multiple sectors, (social welfare, economic health and environmental health) (Pingali 2012).

First, chemical fertiliser production is unsustainable, generating large production costs and expending limited natural resources (Evenson and Gollin 2003). N fertiliser (ammonia, NH_4) is produced by the Haber process, whereby N_2 from the air and H_2 from natural gas is heated and compressed to form liquid NH_4, and is responsible for up to 2 % of annual global natural gas consumption (FAO 2017). Additionally, P (P_2O_5) and K (K_2O) fertilisers are exclusively sourced through finite geological materials, phosphate rock (apatite group $Ca_5(PO_4)_3X$,X = F, Cl, Br or OH) and potash (feldspars and felspathoid minerals, chlorides, sylvite (KCl) and sulphides e.g. polyhalite, $K_2Ca_2Mg(SO_4).2H_2O$) respectively (Savci 2012). Existing reserves of phosphate rock are expected to be exhausted in 50 - 100 years and are located in a handful of countries, most notably Morocco, holding 80 % of rock phosphate supplies (Obersteiner et al. 2013). It is thought future changing climate coupled with increased food demands and the imbalanced availability of rock phosphate may cause significant geopolitical difficulties, particularly for countries lacking high purchasing power (Obersteiner et al. 2013; Roy et al. 2016).

Second, chemical fertilisers alter aquatic ecosystems by reducing water quality and availability (Pingali 2012). Precipitation that falls over agricultural land runs into streams and water bodies, entraining nutrients (N,P) from chemical fertilisers (Pretty et al. 2003). This NP-rich leachate influences ecosystems hosted by natural aquatic rivers and coastal regions, in a process termed ‘eutrophication’ (Howarth et al. 2005). Eutrophication, whereby agricultural runoff stimulates growth of large plant, algae and cyanobacteria blooms, results in oxygen depleted waters and in severe cases, hypoxia (Selman et al. 2008). Evidence shows that aquatic systems deprived of oxygen have decreased biodiversity, increased water toxicity, reduced harvestable fish and shellfish and water treatment problems (Hautier, Niklaus, and Hector 2009). Future changing climate is expected to cause large precipitation pattern changes, intensifying the impact of eutrophication and driving a need for reduced chemical fertiliser use (Sinha, Michalak, and Balaji 2017). Concurrent to the environmental impacts of decreased water quality as a result of chemical fertilisers, past research has shown repercussions upon population health.

Past research has revealed that chemical fertiliser use can deplete water quality impacting human health, particularly in Global South regions reliant on ground-water wells. For example, in the agricultural region of the Punjab, India, approximately 94 % of adults and 100 % children are at high risk from chronic nitrate toxicity (Ahada and Suthar 2018). It has been demonstrated that exposure to nitrates and nitrites from chemical fertilisers in ground water supplies can lead to a condition called methemoglobinemia (Fewtrell 2004). Methaemoglobin (MetHb) is formed when nitrate (NO_3^-) oxidises the ferrous iron in haemoglobin (Hb) to the ferric form (Fan, Willhite, and Book 1987). MetHb is unable to bind oxygen, resulting in oxygen deprivation, cyanosis and cerebral anoxia (Curry 1982; Mansouri and Lurie 1993). The last twenty years has seen widespread evidence that chemical fertilisers impact water quality and subsequently the environment and human health. On top of this, agricultural areas impacted by decreased water quality see a concomitant affect upon water availability (Heathwaite 2010).

Third, chemical fertiliser use compromises water availability in croplands (Vorosmarty et al. 2010). Current intensive farming methods impair water availability by decreasing soil water holding capacity and reducing soil organic matter content (Chien, Prochnow, and Cantarella 2009; Thomson, Marschner, and Römheld 1993; Williams et al. 2016). Long term crop experiments in Italy have shown that chemical fertilisers reduced organic matter by up to 20 % over 40 years compared to organic and mixed farming methods (Nardi et al. 2004). The reduction in organic matter alters soil texture, porosity, microbial communities and water holding capacity (Tisdall and Oades 1982). Future climate warming coupled with increased demands for water, threatens water security and consequently food security (IPCC 2018b). Besides significant negative impacts the environment and human health, the socio-economic system behind chemical fertiliser application acts as a poverty trap (Barrett and Bevis 2015).

Finally, the socio-economic impacts upon farmers who buy into the chemical fertiliser industry are unsustainable. A key proportion of the food production industry are small-scale food producers (< 20 ha), constituting 98 % of global farms that cover 53 % of cropland, predominantly in the Global South. (Stevenson et al. 2013). These farmers lack economic purchasing power and are unable to invest in intensive farming fertilisers or crop varieties unless they take out large loans and credit schemes (Graeub et al. 2016). Providing credit or financial hand-outs has been thought to enable small-holders to invest in their farms and escape poverty (Iqbal et al. 2003). However, debt liabilities and subsequently minimal profits can be catastrophic for farmers, approximately 16,000 farmers die by suicide per year India (Merriott 2016). In addition, the agricultural workforce is in decline due to low employment prospects and lack of facilities, increasing rural-urban migration and widening the rich-poor divide (Collier and Dercon 2014). However, in the Himalayan foothills of India, rural-urban migration has been shown to be dependent more on the prospects of urban life rather than the declining nature of rural life (Hoffmann et al. 2019). Future solutions aiming to improve the agriculture production system, must also focus on remedying the dichotomy between rural and urban life (Nations 2015).

A future sustainable agricultural system also warrants improvements within rural populations, such as community empowerment and schemes to enhance farming economies. Although it may be true that these policies are widely promoted by NGOs, to be effective they also require uptake from governments and states worldwide (G. 2015). Some states in India, Bhutan and Nepal are now aiming to for all agriculture to be organic and low-input (Bharucha, Mitjans, and Pretty 2020). The recent interest in agroecology from these regions is opening opportunities for knowledge exchange and learning, potentially generating a structure for disseminating new practices as well as increasing scientific interest in supporting agroecological development.

In conclusion, to achieve 2030 UN SDGs we must address key aspects across the current agricultural production system. There is an urgent need for food production to increase capacity for the future, whilst protecting the environment, 'sustainable intensification' (Garnett et al 2013). Despite consensus that agricultural systems need urgent change, there is a dichotomy as to how transformation can be achieved. One proposal is focused on high technological capital investment strategies largely supported by agribusinesses. On the other hand, investments into enhancing traditional agroecological farming methods now appear the most beneficial for resource poor farmers of the Global South (Foley, Ramankutty, Brauman, Cassidy, Gerber, Johnston, Mueller, O'Connell, et al. 2011; Godfray et al. 2010b). Within both spheres there is a drive for alternative solutions to the use of chemical fertilisers and as such, investments in one will stimulate feedback into improvements in the other. Despite improvements over the last few years for intense high technology farming, the enhancement of agroecology has failed to advance at a similar rate (Altieri and Nicholls 2012; Altieri et al. 2015; Wezel et al. 2009).

Consequently, there is a need for research into developing novel low budget strategies to improve agroecological farming.

1.2.2 Restoring soils with crushed rock

1.2.2.1 Rock weathering

Enhancing soil fertility through the application of crushed rock takes advantage of 'natural' rock weathering reactions that occur at the Earth's surface. Studies of rock weathering tend to differentiate between chemical, physical and biological weathering (Bland and Rolls 1998). Rock weathering via a combination of physical and chemical weathering, is believed to provide the majority of plant nutrients (see Table 1.1, Figure 1.1) (Jenny 1941). New research has shown that some bedrock types contain considerable amounts of N (sedimentary rocks 500 – 600 mg N kg^{-1}, igneous rock < 100mg N kg^{-1}) and that these N-rich rocks are globally widespread (Houlton, Morford, and Dahlgren 2018). Although these rocks can contain N, it is believed that plants source most required N via the activity of soil microorganisms, either indirectly through the pool of available soil N, or, directly through symbiotic relationships with biological-N fixating microorganisms, such as the legume-rhizobia relationship (Zahran 1999). All other essential nutrient elements (P, K and micronutrients) held within rocks are made available through a series of interdependent reactions.

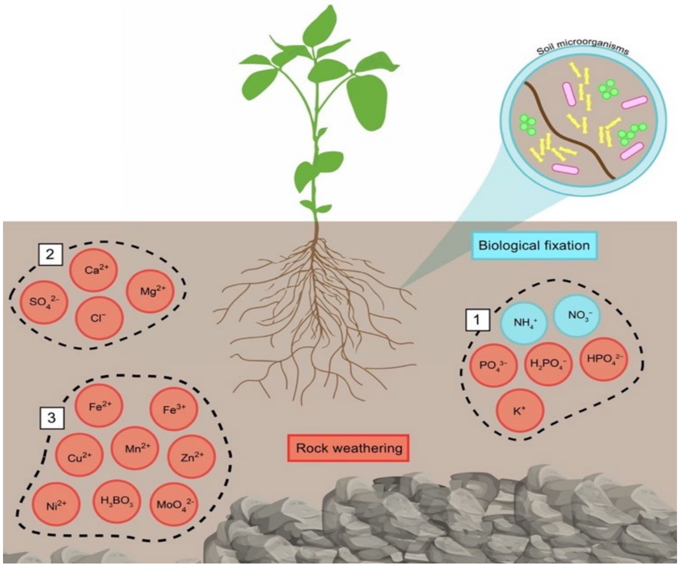


Figure 1.1: Nutrients as absorbed by plant roots within soil matrix. Red: derived from rock weathering, Blue: derived from predominantly biological fixation. Soil microorganisms also enhance availability of P, K, S, Fe. Nutrients are grouped as per plant requirements. Group 1: primary macronutrients, Group 2: Secondary macronutrients, Group 3: Micronutrients. The only nutrient derived wholly from biological fixation is N, however it can very rarely be assimilated through fixation through lightening. This shows the importance of the parent rock material and rock weathering processes for soil fertility.

Table 1.1 : Nutrients required for plants Adapted from: Roy et al. (2006)

Nutrient (Symbol)	***Typical conc. (dried plant matter)***	***Required for***
Nitrogen (N)	1.5%	Constituent of amino acids, protein synthesis and structure, chlorophyll formation,
Phosphorous (P)	0.1 - 0.4%	Vital for nucleic acid formation (DNA, RNA), Cell energy – adenosine triphosphate (ATP) Cell signalling
Potassium (K)	1.0 - 5.0%	Formation of carbohydrates, proteins Regulates plant moisture and water content Enzyme action Contributor to photosynthesis Fruit formation
Sulphur (S)	0.1 - 0.4%	Structure of amino acids (cysteine, methionine) and vitamins Chloroplast growth and function; Fe-S electron transport chain Essential for legumes
Calcium (Ca)	0.2 - 1.0%	Nutrient transport Enzyme activation Photosynthesis Plant structure: cell walls
Magnesium (Mg)	0.1 - 0.4%	Chlorophyll module: energy photosynthesis Critical enzyme reaction activator for C-fixation: RuBisCO, PEPC Protein synthesis: ribosome stabilisation
Chlorine (Cl)	0.2 - 2.0%	Osmosis, Ionic balance, Photosynthesis Stomatal regulation Disease resistance and tolerance
Boron (B)	6 - 60 µg/g	Flowering, fruiting pollination germination, cell division and active salt absorption Plant metabolism – transport of highly polar sugars Cell wall formation, structure
Iron (Fe)	50 - 250 µg/g	Photosynthesis Enzyme co-factor Synthesis of chlorophyll Electron transport
Manganese (Mn)	20 - 500 µg/g	Photosynthesis, building of chloroplasts
Copper (Cu)	5 - 20 µg/g	Photosynthesis, enzymes Manufacture of lignin cell walls Grain production enzymes
Zinc (Zn)	21 - 150 µg/g	Large number of Enzymes, essential role in DNA transcription
Molybdenum (Mo)	below 1.0 µg/g	Enzyme co-factor Amino acids and N metabolism: nitrate reductase and nitrogenase enzyme
Cobalt (Co)	below 1.0 µg/g	Essential for N-fixation and nodule formation
Nickel (Ni)	below 1.0 µg/g	Activation of urease, involved with N-metabolism Enzyme co-factor – Zn substitute

When rock is physically crushed chemical reactions begin almost instantaneously upon wetting. First, the fragmentation of rock particles involves the breaking of bonds and the formation of new surfaces (Keller 1955). Second, mineral grains held within soils are generally subjected to dissolution reactions, but other chemical weathering reactions such as hydration or oxidation can also occur (Anderson, Kussow, and Corey 1985, Montgomery et al. 2000). The coupling of physical and chemical weathering processes are believed to exert a crucial control on the weathering process and subsequent nutrient release (Anderson et al. 2004). The first quantitative 1-D model relating chemical and physical spheroidal weathering showed how dissolution-controlled chemical weathering generated elastic stresses that drove surface fracturing further (Fletcher, Buss, and Brantley 2006). Dissolution rates of minerals depend on four factors; mineral composition, chemistry of reaction solutions, temperature, and biota activity, which are discussed below.

First, dissolution rates are affected by mineral composition and solubility. There are two types of minerals, silicate, and non-silicates. Silicates are the dominant mineral type, forming 90% of the Earth's crust (Taylor 1964). The susceptibility of silicate minerals to dissolution can be predicted by their placing in the 1938 Goldich series, see Figure 1.2 (Goldich 1938). After studying soil profiles, Goldich found that silicate minerals that were formed at higher temperatures and pressures are less stable on Earth's surface than minerals formed at lower temperatures and pressures. High temperature and pressure formed minerals such as olivine are composed of isolated silicate units and are more susceptible due to weaker bonds compared to feldspars, that form silicate sheets (Parker 1970).

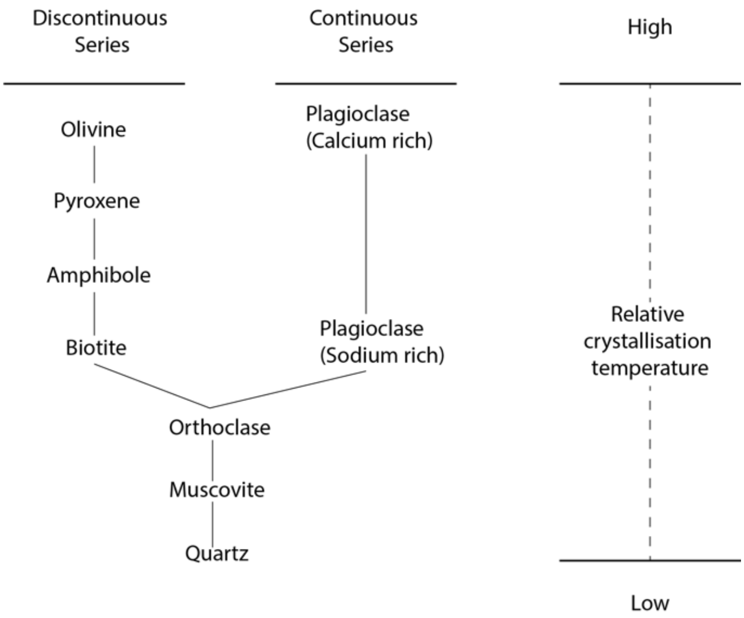
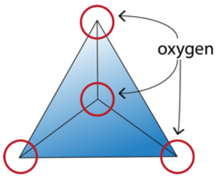


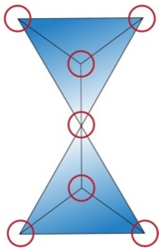
Figure 1.2: Silicate mineral dissolution susceptibility. Adapted from the Goldich reaction series.

The most susceptible minerals to weathering are olivine minerals (Velbel 2009). In these, isolated silica tetrahedron units (SiO_4^{4-}) are held together by the opposing charge of two divalent iron (Fe^{2+}) or magnesium (Mg^{2+}) cations $(Fe,Mg)_2SiO_4$ (Schott and Berner 1985). Less vulnerable to weathering and an important component of soils, sheet silicates (kaolinite and micas) consist of silica tetrahedrons arranged in layers where each unit is sharing three oxygen anions (O^{2-}) (Franzini 1969). The sharing of O^{2-} in these mineral lattices decreases the balance requirement for positively charged cations, which are now only required between each sheet. Thus, bonding between sheets is weak, resulting in well-developed 1-dimensional cleavage as seen in biotites and muscovites and phyllosilicates (small clay minerals) (Jackson 1962). The most resistant silicate mineral, quartz (SiO_2), is formed by silica tetrahedrons arranged in a 3d-framework (Nesbitt, Fedo, and Young 1997). The more resistant the silicate, the fewer cations the minerals contain (Table 1.2).

Table 1.2: Silicate structure geometry

Geometry of linkage of SiO_4 Tetrahedra		**Example mineral**	**Chemical composition**
Isolated tetrahedra: Nesosilicates. No sharing of oxygens between tetrahedra, individual tetrahedra are linked to each other by bonding to cation between them.		Olivine	Unit composition $(SiO_4)^{4-}$ $(Mg,Fe)_2SiO_4$

Double tetrahedra: Sorosilicates consist of one shared oxygen between two tetrahedra, double units are linked to each other by bonding to cations

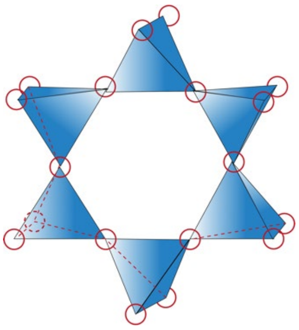


Hemimorphite

Unit composition: $(Si_2O_7)^{6-}$

$Zn_4Si_2O_7(OH)_2 \cdot H_2O$

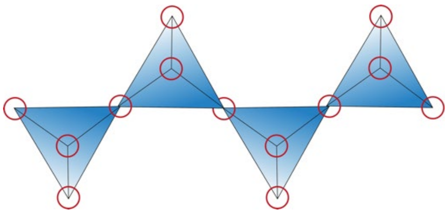
Rings of tetrahedra: Joined by shared oxygens in 3-, 4- or 6-membered rings



Cordierite

$(Mg,Fe)_2Al_3(Si_5AlO_{18})$

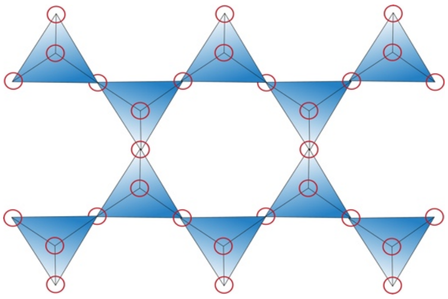
Single chains: Each tetrahedron linked to 2 others by shared oxygens, chains bonded by cations



Pyroxene

$(Mg,Fe)_2Si_2O_6$

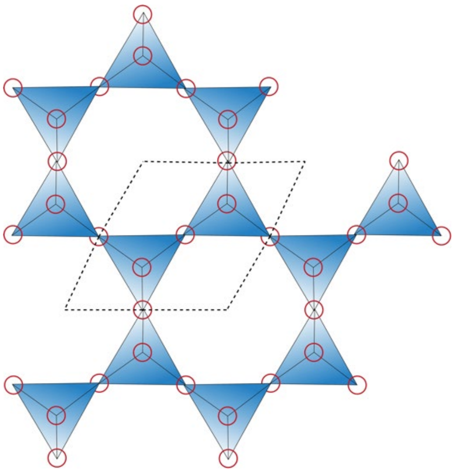
Double chains: Two parallel chains joined by shared oxygens between every other pair of tetrahedra; the other pairs of tetrahedra bond to cations that lie between the cations



Amphibole

$(Mg,Fe,Ca)_{14}(OH)_4Si_{16}O_{44}$

Sheets: Each tetrahedron linked to 3 others by shared oxygens (shown by dashed line), sheets bonded by cations

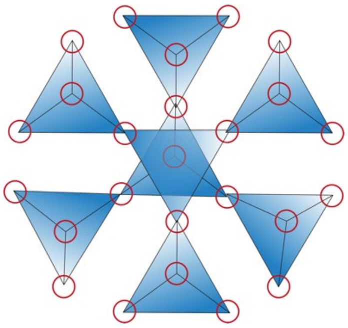


Kaolinite

Aluminium silicate
$Al_2Si_2O_5(OH)_4$

Mica (muscovite)

Potassium-aluminium silicate
$KAl_2(AlSi_3O_{10})(F,OH)_2$ or $(KF)_2(Al_2O_3)_3(SiO_2)_6(H2O)$

Frameworks: Each tetrahedron shares all oxygens with other SiO_4 tetrahedra (in quartz) or AlO_4 tetrahedra		Feldspar (orthoclase) Quartz	Potassium-aluminium silicate $KAlSi_3O_8$ Silicon dioxide SiO_2

Sedimentary rocks, with high carbonate mineral contents have a faster dissolution rate than igneous and metamorphic rocks (Chigira and Oyama 2000). Detrital sedimentary rocks such as conglomerate, breccia and shales are typically composed of minerals that are the most resistant to weathering, (e.g. fragments of quartz and muscovite) together with products of historical weathering (clays) (Sageman and Lyons 2003). Detrital sedimentary rock constituents are generally bound together by cements deposited by percolating solutions that can be particularly liable to chemical weathering (Thompson, Katz, and Krohn 1987). Similarly, authigenic or chemical sedimentary rocks formed through mineral precipitation are highly susceptible to chemical weathering because their key component is water soluble e.g. limestone formed by $CaCO_3$ (Schrag et al. 2013). However, sedimentary rocks like sandstones have grains that are cemented strongly with silicates and are highly resistant to weathering (Turkington and Paradise 2005).

Second, rock dissolution rates are significantly influenced by the chemistry of the solution the minerals are in contact with, particularly pH (Curtis 1990; Cronan 1985). Simple rock dissolution can occur through the hydrolysis of carbonate and silicate minerals (Equation 1.1 and 1.2) (Tranter 2006). However, a more prevalent reaction in the natural environment is acid hydrolysis (Equation 1.3 and 1.4). The acid involved in the dissolution can originate from multiple sources, for example, carbonic acid via dissolution of atmospheric CO_2 and acid generated via other processes such as sulphide oxidation. Carbonation reactions occur in soils because although atmospheric CO_2 concentrations are relatively low (0.04%, 400ppm), plant and microbe respiration increase the CO_2 concentration within the soil solution, reaching up to 1.0 % [CO_2] under normal conditions (Hartmann and Kempe 2008; IPCC 2018b). The increase of CO_2 in the presence of water allows for the formation of carbonic acid (H_2CO_3) in solution. The H_2CO_3 then attacks the mineral lattice of both carbonates and silicates, resulting in further chemical weathering (Bland and Rolls 1998).

Equation 1.1: Carbonate hydrolysis

$$\overbrace{\mathrm{Ca_{1-x}(Mg_x)CO_3}}^{\text{Calcite}}\mathrm{(s)} + \mathrm{H_2O(l)} \leftrightarrow \mathrm{(1-x)Ca^{2+}(aq)} + \mathrm{xMg^{2+}(aq)} + \mathrm{HCO_3^-(aq)} + \mathrm{OH^-(aq)}$$

Equation 1.2: Silicate hydrolysis

$$\overbrace{\mathrm{KAlSi_3O_8}}^{\text{K-Feldspar}}\mathrm{(s)} + \mathrm{H_2O(l)} \leftrightarrow \mathrm{HAlSi_3O_8(s)} + \mathrm{K^+(aq)} + \mathrm{OH^-(aq)}$$

Equation 1.3: Acid hydrolysis of carbonates

$$\overbrace{\mathrm{Ca_{1-x}(Mg_x)CO_3}}^{\text{Calcite}}\mathrm{(s)} + \mathrm{CO_2(aq)} + \mathrm{H_2O(l)} \leftrightarrow \mathrm{(1-x)Ca^{2+}(aq)} + \mathrm{xMg^{2+}(aq)} + \mathrm{2HCO_3^-(aq)}$$

Equation 1.4: Acid hydrolysis of silicates

$$\overbrace{\mathrm{CaAl_2Si_2O_8}}^{\text{Anorthite}}\mathrm{(s)} + \mathrm{2H_2O(l)} + \mathrm{2CO_2(aq)} \leftrightarrow \mathrm{Ca^{2+}(aq)} + \mathrm{2HCO_3^-(aq)} + \mathrm{H_2Al_2Si_2O_8(s)}$$

Third, rock dissolution rates are also affected by soil temperature (Velbel 1990). A higher temperature lowers the necessary activation energy constants for reactions to occur (Keller 1955). The highest rates of rock weathering occur in warm, humid climates with easily weathered bedrock such as tropical karst landscapes, for example Halong Bay Vietnam and Tsingy de Bembaraha Strict Nature Reserve in Madagascar (Cronan 1985; Velbel 1990). The influence of the three abiotic interdependent factors, mineral structure, soil chemistry and temperature upon rock dissolution rates are key to ascertaining the potential of crushed rock as an agricultural soil fertility treatment.

Fourthly, biological activity is a key determinant in rock weathering rates. Plant growth is greatest in the tropics, allowing for maintenance of high soil solution [CO_2], and therefore, high soil [H_2CO_3] (Reich, Walters, and Ellsworth 1997). Through this geochemical ‘hack’, plants and soil microbiota exert biotic control over rock weathering, accessing nutrients that would otherwise remain rock-bound. However, it is not only through this process that rock-bound nutrients become available through biological activity. Biological controls upon weathering are important to take into consideration when assessing the efficacy of crushed rock for agriculture.

1.2.2.2 Biological weathering

The weathering of primary minerals is essential to soil formation, on which the terrestrial biosphere is dependent (Anderson et al. 2004). Biological weathering plays a central role in soil formation and provision of soil nutrients through biogeochemical nutrient cycling (Gadd 2010). Biological weathering is a function of biotic energy expenditure, whereby plant photosynthesis is the principal source of energy for most soil microorganisms (Taylor et al. 2009). The oxidation and respiration of these biological carbon sources result in feedbacks between mineral weathering and the geochemical carbon cycle (Leake et al. 2018). An understudied and overlooked area in the use of crushed rock to boost soil fertility in farming is the importance of biological weathering. Biological weathering is driven by plants and mycorrhizal organisms.

Plants are the primary force of biotic weathering (Lucas 2001). Plants adjust the soil solution in two ways. First, plants alter the pH of the soil solution which stimulates rock weathering by releasing protons (H^+) and hydroxyl ions (OH^-), either raising or lowering pH by up to 2.5 units (Lucas 2001). As the root excretes H^+, it exchanges basic cations (Mg^{2+}, Ca^{2+}, NH_4^+, K^+ etc) to maintain charge balance and organic acids (e.g. acetic acid (CH_3COOH)) (Briskin 1994). Second, plants can adjust the complexing capacity of soil, by enhancing the formation of metal-organic complexes (M.G. van den Berg 1984). Organic acids exuded from roots act as chelators, binding and mobilising less insoluble metals (Fe, Cu, P) (Meagher 2000; Jones, Darah, and Kochian 1996). Two key phytochelators are malate and citrate which are released up to 30 times their normal rate in times of micronutrient deficiency (Jones and Darrah 1995). When chelators are unavailable metal oxides are immobilized as secondary minerals, removing once available ions and nutrients (Lucas 2001). Research has shown that soybeans exude organic acids when experiencing P deficiency and Al toxicity, two common inseparable limiting factors for crop productivity on agricultural soils (Dong, Peng, and Yan 2004). The organic acid anions act as a detoxification mechanism, binding toxic cations (Al^{3+}), forming sufficiently strong complexes to protect plant roots (Ma, Ryan, and Delhaize 2001).

Bacteria and fungi are geoactive agents, actively facilitating the process of biogeochemical reactions and rock weathering. Microbes drive rock weathering by three proposed mechanisms. First, microbes may weaken physical rock structure by forming colonies or biofilms on rock surfaces or in crevices, resulting in bio-corrosion, bio-erosion and boring (Barker and Banfield 1998, 1996). Second, microbes may intensify chemical weathering by decreasing the pH of the soil environment by the acidification of organic acids secreted by microorganisms and CO_2 release from microbial respiration onto rock surface particles (Ehrlich 1998). Third, microorganisms mine for specific elements for nutritional purposes to produce complicated organic ligands to acquire nutrition from mineral-bound elements (Lian et al. 2008). Microorganisms capable of mining for mineral bound elements include bacteria (e.g. iron-oxidizing and -reducing, manganese-oxidising and -reducing), cyanobacteria, prokaryotes and eukaryotes (Gadd 2010; Fierer, Bradford, and Jackson 2007). As well as performing a key role in biological rock weathering, soil microorganisms establish and maintain other important aspects of soil fertility such as supporting the plant available pool of soil-N and improving soil organic matter concentrations.

The available pool of soil-N can be increased through biological nitrogen fixation (BNF), whereby specialised microbes use a nitrogenase enzyme to catalyse the conversion of atmospheric N_2 to ammonia NH_3 (Beijerinck 1901). Plants can then assimilate NH_3 to produce nitrogenous biomolecules, amino acids, proteins and chlorophyll (Postgate 1982). BNF occurs in two ways dependent on the soil habitat, either free-living or symbiotic fixation, as shown in Figure 1.3 (Smercina et al. 2019). In free-living BNF, N-fixation is achieved by a variety of N-fixers living within the soil community, however in symbiotic N fixation this is performed by unique rhizobia living within the nodule population (Vitousek et al. 2002). Free-living BNF is supported by DOC in the soil, whereas symbiotic N-fixers receive a supply of simple C-compounds directly from the host plant (Reed, Cleveland, and Townsend 2011). Nutrients necessary to support free-living N-fixation must be acquired by the N-fixer (e.g. P, Fe, Mo and V), where in symbiotic N-fixation, these nutrients must be provided by the plant (Pii et al. 2015; Rashid et al. 2016). Both forms of BNF require soils rich in micronutrients (Bøckman 1997). This is because nitrogenase is a metalloenzyme, consisting of two proteins, most commonly a molybdenum iron protein (Protein 1) (MoFe, Nif) that binds N_2 (dinitrogenase reductase) and a smaller iron protein (Protein 2) that acts as an electron donor to protein 1 (nitrogenase reductase) (Lea 1997). Alternative nitrogenases that contain vanadium (VFe, Vnf) or heterometal independent forms (Fe-only, Anf) in the larger subunit have been identified (Mcglynn et al. 2013). Reed, Cleveland, and Townsend (2011) showed that the rates for free living and symbiotic fixation were similar across all biomes, suggesting both mechanisms play an important role in soil N availability.

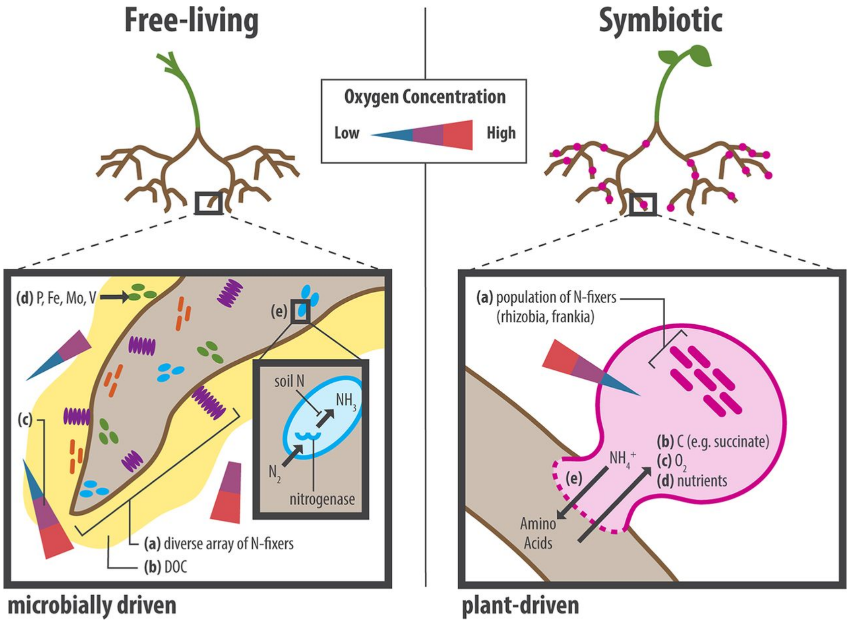


Figure 1.3: The two mechanisms behind microbial N fixation within the soil (Smercina et al. 2019)

Both methods of BNF have been of particular interest for low-input agroecological crop production due to a potential reduction in chemical fertilisers. (Jensen and Hauggaard-Nielsen 2003). BNF is a sustainable source of N within agricultural cropping systems for two reasons. First, atmospheric N_2 is a renewable resource and secondly, N production via BNF is driven by photosynthetic energy (Ledgard and Steele 1992). When compared to N-fertiliser production via the energy-intensive Haber-Bosch process, BNF is virtually ‘free’ (Jensen and Hauggaard-Nielsen 2003; Bøckman 1997). There has been success in Brazil where farmers have focused on improving BNF soybean production. Soybeans are Brazil’s foremost agricultural export - the country produces 20 % of the world’s soybeans (32.7 x 10^6 Mg) yet farmers in Brazil rely on minimal N-fertiliser investment, saving over US$2.5 billion per year (Alves, Boddey, and Urquiaga 2003). As well as maintaining the availability of N through symbiosis, microorganisms are also important in the soil C-cycle.

The second way soil microbes improve soil fertility is through improving the organic matter status of soils. SOM cycling is controlled by the controlled by the activity of rhizosphere microbiota (Kuzyakov and Cheng 2001). Soil microorganisms use organic compounds in SOM as C sources for metabolism, breaking down complex organic compounds e.g., cellulose and lignin in decaying plant residues into simple organic compounds. The stable fraction of soil organic matter, humus, is associated with mineral particles forming humate-clay complexes, acting as a slow-release source of carbon and minerals ‘the recalcitrant fraction’ (Schmidt et al. 2011). Completing the SOM cycle, microbial products are themselves important input components (Kögel-Knabner 2002).

SOC and SOM are essential for achieving crop yields, where the critical threshold for productive soils is 2 %, and anything below this value is categorised as a desert (Oldfield, Bradford, and Wood 2019). SOM affects three key soil properties. First, SOM promotes soil fertility by increasing nutrient retention. SOM can increase nutrient retention by providing cation exchange sites, acting as a reserve for N, P, S and micronutrients, which are eventually released through SOM mineralisation (Garcia-Pausas and Paterson 2011; Clemente, Escolar, and Bernal 2006). Second, SOM improves soil structure by promoting aggregation allowing for efficient drainage, water holding capacity and aeration. Last, SOM minimises the loss of topsoil via erosion in two ways by improving drainage decreasing water runoff and by being preferentially removed by surface water runoff due to low density and higher presence in the top layer (Tisdall and Oades 1982). Losing small quantities of SOM, rather than sediment-bound mineral nutrients, in surface water runoff maintains soil fertility (Boyle, Frankenberger, and Stolzy 1989). This is because SOM production is a much faster process than the production of other key soil fractions, such as rock-bound mineral nutrients. SOM decomposition and SOC storage is also fundamental to C emissions and future climate projections, whereby SOC stores are at risk of release if soils are poorly managed (Kirschbaum 1995).

The activities of microbes in biological rock weathering are now becoming recognised as geochemically significant. The field of geomicrobiology has grown steadily over the last few decades, coinciding with the development and advancement of microbiological research methods (Sylvia et al. 2005). There has been a dramatic rise in research into sustainable agriculture, with research paper output doubling from 983 articles in 2014 to 2119 articles in 2018. This substantial increase has largely been driven by improved technology, changing research priorities and global policies (UN SDGs and COP21). Sustainable agricultural research is currently focused on employing novel crop genetic modifications, microbial inoculants, land management and irrigation strategies with heavy technological investment (Altieri, Nicholls, and Montalba 2017).

One such method of potential soil improvement is the application of microbial inoculants. Soil microorganisms can improve agricultural soils through activities, e.g.

increasing nutrient availability, pathogen suppression and ethylene reduction (Kaminsky et al. 2019). Microbial inoculants are a rapidly growing field, achieving large financial investment, however their success remains unpredictable (Bhardwaj et al. 2014). Although thought to be fairly novel, microbial inoculants have been used since the 19th Century, whereby in the USA it was advised that legume seeds were 'naturally inoculated' with farm soil prior to planting (Smith 1992a). Although biological weathering processes have potential to improve soil nutrient content, without sufficient soil minerals for biological reactions, microbial inoculation alone may be insufficient for nutrient enrichment, thus highlighting a potential need for rock minerals. As well as nutrient enrichment, weathering mechanisms are now being employed as a novel strategy to reduce atmospheric CO_2, 'enhanced weathering' (Beerling et al. 2020).

1.2.2.3 Chemical weathering and Carbon

Chemical weathering products are a known deposit of C within the carbon cycle (Goudie and Viles 2012, Maher and Chamberlain 2014). Carbonate and silicate weathering both contribute to the short term Soil C (inorganic and organic C) store in two ways (Dessert et al. 2003). First, inorganic C- containing minerals form through weathering and acid hydrolysis (e.g., Equation 1.5, 1.6). Second, rock-bound nutrients stimulate soil biota increasing the organic C component (Hartmann, West, Renforth, Kohler, et al. 2013). Long term C storage in rocks occurs across geological timescales, spanning both silicate and carbonates (Berner 1992; Raiswell and Berner 1987).

Equation 1.5: Calcium silicate weathering (acid hydrolysis)

$$2CO_2 + 3H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4$$

Equation 1.6: Calcium carbonate precipitation

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

'Enhanced weathering' involves the application of crushed silicate rock to agricultural land to capture C, utilising weathering and precipitation chemistry (Figure 1.4) (Hartmann, West, Renforth, Kohler, et al. 2013; Moosdorf, Renforth, and Hartmann 2014; Schuiling and Krijgsman 2006; Lewis et al. 2021; Kelland et al. 2020; Beerling et al. 2018a; Beerling et al. 2020). As silicate rocks weather, the binding cation is released, e.g., calcium silicate $CaSiO_3$

releases Ca^{2+}. These cations then go on to precipitate into secondary products within the soil, increasing soil-C, e.g., Equation 6, $CaCO_3^-$. Enhanced weathering not only focuses on increasing the soil-C store, but also the ocean C stocks (Hartmann, West, Renforth, Köhler, et al. 2013). The weathering products cations (Ca^{2+}) and bicarbonates (HCO_3^-) that can be washed off due to precipitation and transported by rivers or carried within aeolian dust out to the ocean where two drawdown mechanisms can occur (Taylor et al. 2016). First, they can remain in the dissolved phase and are stored in the dissolved ocean carbon pool. Second, the bicarbonate ions [HCO_3^-] can precipitate e.g., by growth of diatoms, foraminifera, corals. Although for every two CO_2 drawdown, only one C is stored via precipitation, and another is released following silicate weathering. The flux of [HCO_3^-] has the potential to improve ocean alkalinity, increasing ocean pH and reducing the potential for harmful toxic algal blooms (Hartmann, West, Renforth, Kohler, et al. 2013).

The Hubbard Brook experiment assessed enhanced weathering of calcium silicates over a 12 year field experiment (Peters et al. 2004; Shao et al. 2016). It was estimated following water and soil chemistry analysis, that the application of wollastonite powder $CaSiO_3$ achieved a CO_2 capture efficiency of ~60 % (Hartmann and Kempe 2008; Hartmann, West, Renforth, Kohler, et al. 2013; Beerling et al. 2018a). Using the efficiency data from the experiment, Table 1.3 shows the potential C capture if wollastonite powder was applied to Indian and UK degraded crop land. When applied at a rate reasonable for farmers of 2.0 T ha^{-1}, CO_2 drawdown of 176.4 million t CO_2 ha^{-1} could be achieved over all 147 million ha of degraded Indian agricultural land. These theoretical calculations suggest that the addition of silicate rock powders could provide a viable potential mechanism for CO_2 drawdown in agricultural land.

Table 1.3: Wollastonite potential C capture of crushed wollastonite if applied for 12 years cross agricultural land in India – 147.00 M ha degraded soils, UK – 9.34 M ha degraded soils.

Crushed rock application rate (T ha^{-1})	**Potential C capture** (T CO_2 ha^{-1})	**Potential C capture for Indian agricultural land** (MT* CO2 ha^{-1})	**Potential C capture for UK agricultural land** (MT CO2 ha^{-1})
0.5	0.3	44.1	2.8
1.0	0.6	88.2	5.6
2.0	1.2	176.4	11.2
5.0	3.0	441.0	28.0
10.0	6.0	882.0	56.0

*MT = Million Tonne (metric, 1000 kg)

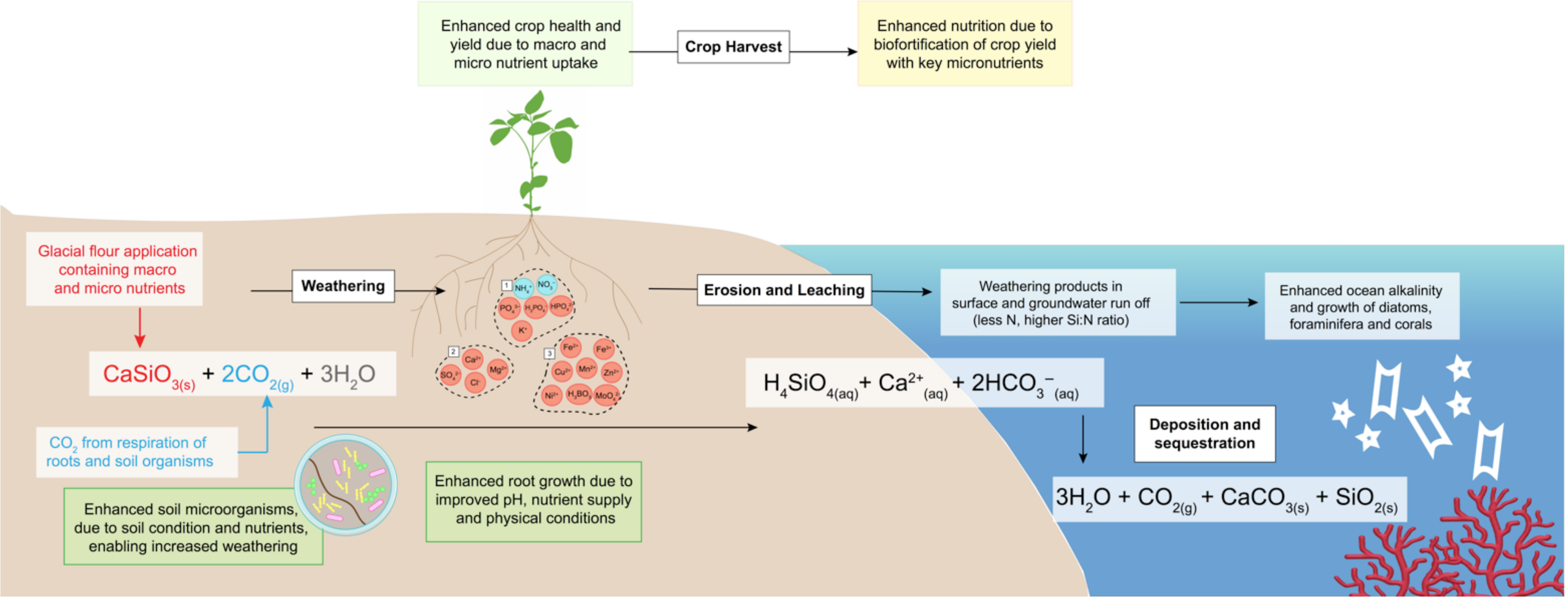


Figure 1.4: Conceptual model of Enhanced Weathering, C-capture. Indicating the routes of weathering and potential reactions. Adapted from Beerling, 2018.

As well as the potential CO_2 drawdown, the application of crushed rock to agricultural land may also reduce fluxes of N_2O (a more potent greenhouse gas) (Kantola et al. 2017). This effect has been shown when agricultural lime is commonly applied as a soil buffer (Bakken et al. 2012; Borken and Brumme 1997; Brumme and Beese 1992). The mechanisms of N_2O reduction through liming are not well understood but is thought to be due to the increased microbial N-fixation (Bakken et al. 2012; Qu et al. 2014). There is evidence to suggest that application of crushed silicate rocks may cause a similar impact to agricultural lime ($CaCO_3$) (Beerling et al. 2018b; Leake et al. 2018). Furthermore, crushed rock may provide key micronutrients for microorganisms N-fixation enzymes, nitrogen reductase and Ni-dependent urease all require available molybdenum (Mo) and nickel (Ni) (Bambara and Ndakidemi 2010; de Macedo et al. 2016). However, this is a key research gap within crushed rock literature. Nonetheless, despite potential positive effects, enhanced weathering remains limited by four key factors; 1) large application rates, 2) energy / C requirement to crush and transport rock, 3) temperature / climate, and 4) metal contamination.

First, the application of crushed rock to land investigated so far has been variable ranging from 0.5 - 100 T ha^{-1} with high application rates (> 20 T ha^{-1}) commonly investigated (Hartmann and Kempe 2008; Hartmann, West, Renforth, Kohler, et al. 2013; Beerling et al. 2018a). Application rates (>5 T ha^{-1}) are seen as largely impractical for farmers and are well above the standard liming rate addition of 2 T ha^{-1}. Achieving target CO_2 drawdown effects requires either large quantities of rock or the rock being crushed to a finer powder to improve reaction potential. Mitigating this requires crushing and transportation, the second limitation to the application of crushed rock. It is believed that crushing rock to required particle size (< 200 μm) will have significant production, manufacturing and application associated costs, both economic and in terms of C-emissions (Beerling et al. 2020; Beerling et al. 2018b). Second, although some research suggests that there are prospective large gains in C-capture for UK and higher latitude degraded soils (11.2 million t CO_2 ha^{-1}, at an application rate of 2.0 T ha^{-1}) (Peters et al. 2004; Shao et al. 2016), the potential of enhanced weathering in these climates is significantly limited (Renforth 2012; Sukstorf, Bennike, and Elberling 2020). Lower average temperatures and precipitation result in much slower weathering reactions (Edwards et al. 2017; Curtis 1990; Velbel 1990). This suggests crushed rock may be more effective in low latitude soils with high precipitation. Finally, the adoption of enhanced weathering is limited by potential metal contamination dependent upon the source silicate rocks.

1.2.2.4 The history of crushed rock farming

Research for alternatives to chemical fertilisers began in the late 1800's by Dr Julius Hensel (Hensel 1894a). Hensel applied the theory of pedogenesis, the process of soil formation. The formation of soil relies on multiple components, one important element is the action of parent rock weathering to generate soil nutrients (Jenny 1941). In an attempt to kick-start soil evolution on agricultural lands, Hensel applied freshly crushed rock as a strategy to rejuvenate soils (Ramos, de Mello, and Kautzmann 2014). He achieved success in Germany in 1890 and suggested the application of crushed rock to tobacco crop lands in Virginia, USA as an alternative to expensive wood ash (Hensel 1894a). Despite positive effects at the time, Hensel was lobbied by the agricultural chemicals industry, his house was burnt down and research into crushed rock was abandoned (Franck 1993). Subsequently, the chemical fertiliser industry boomed, and agricultural intensification began. Numerous reports have stressed the necessity for transformation of the global food system, frequently advocating agroecological methods as a solution (McIntyre 2009; De Schutter 2010). However, critics claim that agroecological methods may have lower yields and would need more land to produce the same amount of food, minimising any advantageous environmental benefits (Trewavas 2001). To establish crushed rock as a potential agroecological method within future sustainable food production, the factors limiting yields of crushed rock need to be fully understood (Manning 2010).

A full literature review of past crushed rock crop yield investigations was performed, resulting in 49 observations from 11 publications for comparison (Table 1.4). Past research investigating the effect of crushed rock upon crop yield tends to show a positive yield response to rock application, 84 % positive observations. However, the observations have a large range, from -66 to +146 % change in yield, (Figure 1.5) indicating that there may be features of crushed rock that result in a more positive impact on crop yield.

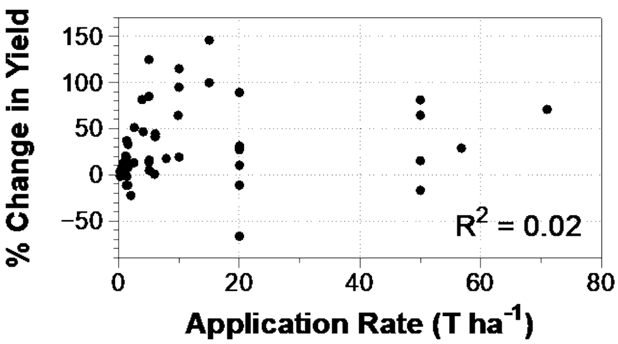


Figure 1.5: % Change in yield and crushed rock application rate for all observations included in the literature review.

Table 1.4: Observations from Crushed Rock literature

Author	Date	Rock	Rock type	Crop type	Field or lab	Application rate (T ha^{-1})	Particle size (µm)	n	Change in yield compared to control (%)	Change in yield per T applied (% (T ha-^{1})$^{-1}$)	Change in yield scaled by particle size factor (% (T ha-^{1})$^{-1}$)
Sanz-scovino + Rowell	1988	Sanidine Feldspar	Igneous	Grass	Field	0.28	75	5	-1.4	-4.91	-0.13
Sanz-scovino + Rowell	1988	Sanidine Feldspar	Igneous	Grass	Field	0.56	75	5	9.6	17.1	0.44
Sanz-scovino + Rowell	1988	Sanidine Feldspar	Igneous	Grass	Field	1.10	75	5	20.6	18.3	0.47
Coroneos et al.	1995	Quarry Granite	Igneous	Legume	Lab	20.0	70	3	89.3	4.53	0.05
Coroneos et al.	1995	Quarry Granite	Igneous	Grass	Lab	20.0	70	3	31.4	1.57	0.02
Hisinger et al.	1996	Quarry Granite	Igneous	Cereal	Lab	0.21	500	3	3.4	16.2	3.74
Hisinger et al.	1996	Quarry Granite	Igneous	Cereal	Lab	0.83	500	3	2.3	2.73	0.63
Hisinger et al.	1996	Quarry Granite	Igneous	Cereal	Lab	2.50	500	3	13.1	5.22	1.21
Hisinger et al.	1996	Quarry Granite	Igneous	Cereal	Lab	5.00	500	3	13.6	2.73	0.63
Hisinger et al.	1996	Quarry Granite	Igneous	Cereal	Lab	10.00	500	3	19.3	1.93	0.45
Bakken et al.	2000	Adularia fucoids	Sedimentary	Grass	Field	0.77	662	15	3.3	4.23	1.33
Bakken et al.	2000	Nepheline syenite mine tailings	Igneous	Grass	Field	1.07	500	15	15.4	14.4	1.85
Bakken et al.	2000	Biotite Schists	Metamorphic	Grass	Field	0.75	750	15	12.5	5.58	0.72

Author	Date	Rock	Rock type	Crop type	Field or lab	Application rate	Particle size	n	Change in yield compared to control	Change in yield per T applied	Change in yield scaled by particle size factor
						(T ha^{-1})	(µm)		(%)	(% (T ha-^{1})$^{-1}$)	(% (T ha-^{1})$^{-1}$)
Bakken et al.	2000	Epidote Schists quarry waste	Metamorphic	Grass	Field	2.24	750	15	12.5	16.6	5.97
Bakken et al.	2000	Carbonatites	Igneous	Grass	Field	1.41	750	15	12.4	8.82	3.17
Bolland + Baker	2000	Quarry Granite	Igneous	Cereal	Field	2	500	4	-22.4	-11.2	-2.58
Bolland + Baker	2000	Quarry Granite	Igneous	Cereal	Field	20		4	-66.3	-3.31	-0.76
Badr et al.	2006	Orthoclase Feldspar	Igneous	Fruit	Field	1.29	175	3	37.2	28.8	1.85
Badr et al.	2006	Orthoclase Feldspar	Igneous	Fruit	Field	2.57	175	3	51.4	19.9	1.28
Badr et al.	2006	Orthoclase Feldspar	Igneous	Fruit	Field	3.86	175	3	81.6	21.1	1.36
Mohammed et al. (Artificial soil)	2014	Microcline	Mineral	Vegetable	Lab	1.26	100	3	18.9	15.1	0.39
Mohammed et al. (Artificial soil)	2014	Microcline	Mineral	Vegetable	Lab	5.05	100	3	16.2	3.20	0.08
Mohammed et al. (Artificial soil)	2014	Biotite	Mineral	Vegetable	Lab	1.51	100	3	7.65	5.07	0.13
Mohammed et al. (Artificial soil)	2014	Biotite	Mineral	Vegetable	Lab	6.04	100	3	44.5	7.36	0.19

Author	Date	Rock	Rock type	Crop type	Field or lab	Application rate (T ha^{-1})	Particle size (µm)	n	Change in yield compared to control (%)	Change in yield per T applied (% (T ha-^{1})$^{-1}$)	Change in yield scaled by particle size factor (% (T ha-^{1})$^{-1}$)
Mohammed et al. (Natural soil)	2014	Microcline	Igneous	Vegetable	Lab	1.26	100	5	-11.3	-8.96	-0.23
Mohammed et al. (Natural soil)	2014	Microcline	Igneous	Vegetable	Lab	5.05	100	5	4.84	0.96	0.03
Mohammed et al. (Natural soil)	2014	Biotite	Metamorphic	Vegetable	Lab	1.51	100	5	33.1	21.9	0.56
Mohammed et al. (Natural soil)	2014	Biotite	Metamorphic	Vegetable	Lab	6.04	100	5	41.1	6.81	0.18
Mohammed et al. (Natural soil)	2014	Nepheline syenite	Igneous	Vegetable	Lab	1.48	100	5	-11.3	-7.63	-0.19
Mohammed et al. (Natural soil)	2014	Nepheline syenite	Metamorphic	Vegetable	Lab	5.91	100	5	0.81	0.14	0.004
Dahlin & Stenberg	2017	Pyroxene andesite	Igneous	Legume	Lab	50	1000	4	81.3	1.63	0.79
Dahlin & Stenberg	2017	Pyroxene andesite	Igneous	Legume	Lab	50	1000	4	64.7	1.29	0.63
Dahlin & Stenberg	2017	Pyroxene andesite	Igneous	Grass	Lab	50	1000	4	15.4	0.31	0.15
Dahlin & Stenberg	2017	Pyroxene andesite	Igneous	Grass	Lab	50	1000	4	-16.7	-0.33	-0.16
Manning et al.	2017	Syenite	Igneous	Vegetable	Lab	1.08	75	10	9.68	8.96	0.11
Manning et al.	2017	Syenite	Igneous	Vegetable	Lab	7.87	75	10	17.7	2.25	0.03

Author	Date	Rock	Rock type	Crop type	Field or lab	Application rate (T ha^{-1})	Particle size (µm)	n	Change in yield compared to control (%)	Change in yield per T applied (% (T ha-^{1})$^{-1}$)	Change in yield scaled by particle size factor (% (T ha-^{1})$^{-1}$)
Manning et al.	2017	Syenite	Igneous	Vegetable	Lab	56.8	75	10	29.0	0.51	0.007
Manning et al.	2017	Syenite	Igneous	Vegetable	Lab	4.06	75	10	46.8	11.5	0.15
Manning et al.	2017	Phlogopite mica	Mineral	Vegetable	Lab	1.35	75	10	-1.61	-1.19	-0.02
Manning et al.	2017	Phlogopite mica	Mineral	Vegetable	Lab	9.84	75	10	64.5	6.56	0.08
Manning et al.	2017	Phlogopite mica	Mineral	Vegetable	Lab	71	75	10	71.0	0.99	0.01
Priyono and Arifin	2012	Basalt	Igneous	Grass	Lab	5	50	2	125	25.0	0.00
Priyono and Arifin	2012	Basalt	Igneous	Grass	Lab	10	50	2	115	11.5	0.00
Priyono and Arifin	2012	Basalt	Igneous	Grass	Lab	15	50	2	100	25.0	0.00
Priyono and Arifin	2012	Basalt	Igneous	Legume	Lab	5	50	2	85	17.0	0.00
Priyono and Arifin	2012	Basalt	Igneous	Legume	Lab	10	50	2	95	9.50	0.00
Priyono and Arifin	2012	Basalt	Igneous	Legume	Lab	15	50	2	146	9.73	0.00
Wang	2010	Gneiss	Metamorphic	Grass	Lab	20	2000	5	-11.1	-0.56	-0.56
Wang	2010	Gneiss	Metamorphic	Vegetable	Lab	20	2000	5	10.4	0.52	0.52
Wang	2010	Gneiss	Metamorphic	Legume	Lab	20	2000	5	27.3	1.36	1.36

Past crop growth investigations (Table 1.4) have been performed on a variety of selectively crushed rock sources from around the world (75 % of studies), however some research has focused on the potential of quarry or mining waste (25 % of studies) as opposed to selectively milling crushed rock, in an effort to utilise waste resources and lower energy costs (Priyono and Gilkes 2008a). When comparing the % change in yield per tonne (T) of crushed rock applied, selectively chosen rock increased yields by double the quantity compared to quarry or mining waste (7.4 ± 1.4 % per T ha^{-1}) compared to quarry or mining waste (3.7 ± 2.1 % per T ha^{-1}). Some crushed rock research opposes the use quarry or mine waste, claiming it has lower effectiveness than other rock types (Bakken et al. 2000). However, the analysis of observations in this study, indicates that when the change in yield is scaled by particle size, both rock sources achieve a similar increase in crop yields (Figure 1.6a and b, Table 1.5). This suggests that particle size is a dominant feature in determining the potential for crushed rock application upon soils.

Table 1.5 Rock source and particle size factor scaling

Rock source	Change in yield above control	Particle size range	Particle size factor	Scaled change in yield
	(% (T ha^{-1})$^{-1}$)	(μm)		(% (T ha^{-1})-^{1})
Selected rock	7.4 ± 1.4	50 - 2000	0.169	0.5 ± 0.2
Quarry / mine	3.7 ± 2.1	70 - 500	0.172	0.5 ± 0.5

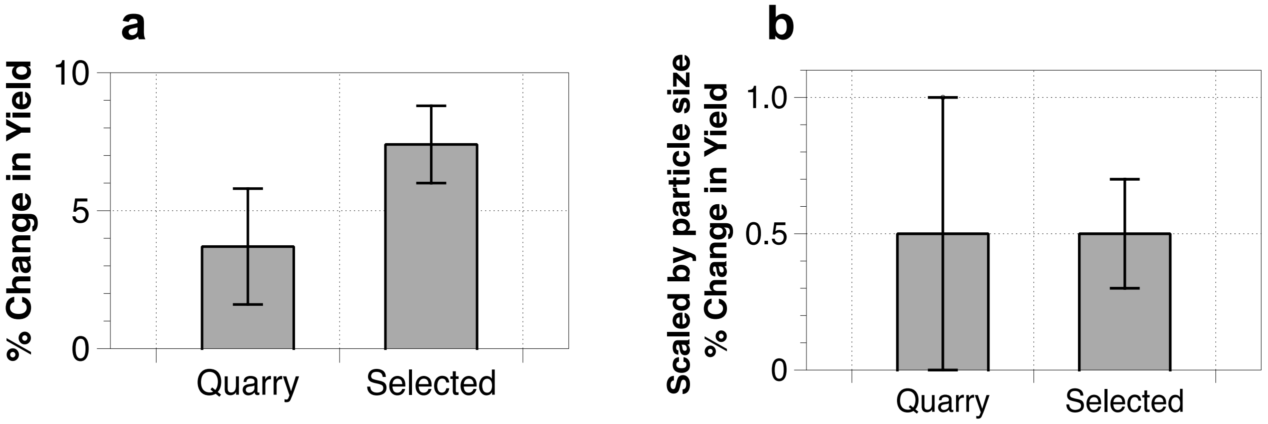


Figure 1.6 a) % Change in Yield per T of applied crushed rock for quarry and mine waste compared to selectively crushed rock. **b)** % Change in Yield per T of applied crushed rock scaled by particle size for quarry and mine waste compared to selectively crushed rock

Table 1.6 Particle size groups and mean change in yield above control

Particle size range	Change in yield above control	n
(μm)	*(% per T ha^{-1})*	
0 - 99	7.67 ± 1.74	15
100 - 499	9.02 ± 2.80	16
500 - 999	4.40 ± 2.50	10
1000 +	0.60 ± 0.30	7

Particle size appears to exert a strong influence on crushed rock-achieved crop yields. Table 1.6 outlines the four main groups of particle sizes that were applied within the observations across crushed rock literature. The two smallest particle sizes groups 0 – 99 μm and 100 – 499 μm were the most effective, achieving a similar response, 7.67 ± 1.74 (% (T ha^{-1})$^{-1}$ and 9.02 ± 2.80 % (T ha^{-1})$^{-1}$ respectively. Past observation data indicates that as particle size increases, the yield response decreases, for example for crushed rock particles > 1000 μm, there is only a 0.60 ± 0.30 % per T ha^{-1} change in crop yield. This is likely because when applied at the same rate, the smaller particle sized crushed rock will have greater surface area than larger particles and thus, larger potential reaction surfaces for rock weathering dissolutions (Schott and Berner 1985). However, past research has also investigated the impact of crop growth using an array of different crop types.

Yield success of crushed rock appears dependent on crop type in addition to crushed rock particle size as shown in Table 1.7. Normalised change in yields, indicates that both cereals and vegetables crops were below the mean (6.94 % per T ha^{-1}), therefore this suggests these crop types may not be the most ideal for crushed rock treatment. However, fruit trees, grasses and legumes showed an above average response to crushed rock (Table 1.4). Fruit crops appear to undergo the most dramatic increase in crop yields, 23.3 ± 3.9 % per T ha^{-1}, however these observations also had the smallest mean particle size 175.0 ± 0.0 μm (n = 3). In comparison, the crushed rock applied within legumes and grasses investigations had a much larger mean particle size, greater than five times that of the rock applied to fruit trees (Table 1.4). Additionally, despite a large particle size (> 500 μm), grasses and legumes increase crop yields. This is likely due to similar nutrient requirements of these crops in comparison to vegetables and cereal crops.

Table 1.7 Crop type and the change in yield above control (% per T ha^{-1}) and mean particle size of the observations from literature (values presented as the mean of the dataset, error is the standard deviation to 3 significant figures)

Crop type	Change in yield above control	Mean Particle size	Normalised change in yield	Normalised particle size	n
	(% per T ha^{-1})	*(µm)*			
Cereal	-2.05 ± 7.71	1480 ± 130	-1.01 ± 0.46	0.73 ± 0.15	11
Fruit	23.3 ± 3.9	175 ± 30	1.85 ± 0.38	0.06 ± 0.01	3
Grass	8.92 ± 8.25	570 ± 150	0.22 ± 0.18	0.27 ± 0.15	15
Legume	7.27 ± 5.49	894 ± 390	0.04 ± 0.01	0.43 ± 0.26	7
Vegetable	4.32 ± 7.38	225 ± 105	-0.29 ± 0.12	0.09 ± 0.02	18

Legume and grasses may be crops with greater susceptibility for success following crushed rock application, this is potentially due to their nutrient demands (Baylor 1974). Legumes and grasses both have minimal N demands, but need P and K, compared with other crop types, such as cereals and vegetables, which have high N, P and K needs (Macy 1936). Past crushed rock research suggests that N is unavailable or present in very low concentrations in crushed rock (Bolland and Baker 2000a). However, low N input is likely not to be an issue for leguminous crops, that form a symbiotic relationship with rhizobium microorganisms, exchanging biologically fixed N for plant sugars (Ledgard and Steele 1992). Conventional large scale agriculture tends to grow legumes such as soybeans as a cash crop for bio-oils, however, agroecological movements use legumes such as soybeans for food and clover, mixed with different grass species as a key cover crop during inter-cropping fallow years to improve soil N (Altieri 2000; Altieri et al. 2015). Past crushed rock crop trials have clearly demonstrated the importance of particle size upon rock weathering rates. They have also indicated that legumes may be the most effective crop for crushed rock treatment. However, there are further factors that control rock weathering rates that are determined by chemical and biological soil system interactions.

1.2.3 Potential sources of crushed silicates

The effectiveness of the application of crushed silicate minerals for the purpose of boosting soil fertility and enhancing weathering is strongly influenced by the type of minerals applied. Past research into both soil fertility and enhanced weathering has focused on the application of olivine, a fast-weathering magnesium iron silicate mineral, already mined for use in steel works, aluminium foundry works and is marketed as the ideal rock for Finnish sauna stoves because of its resistance to repeated heating and cooling (Schuiling and Krijgsman 2006).

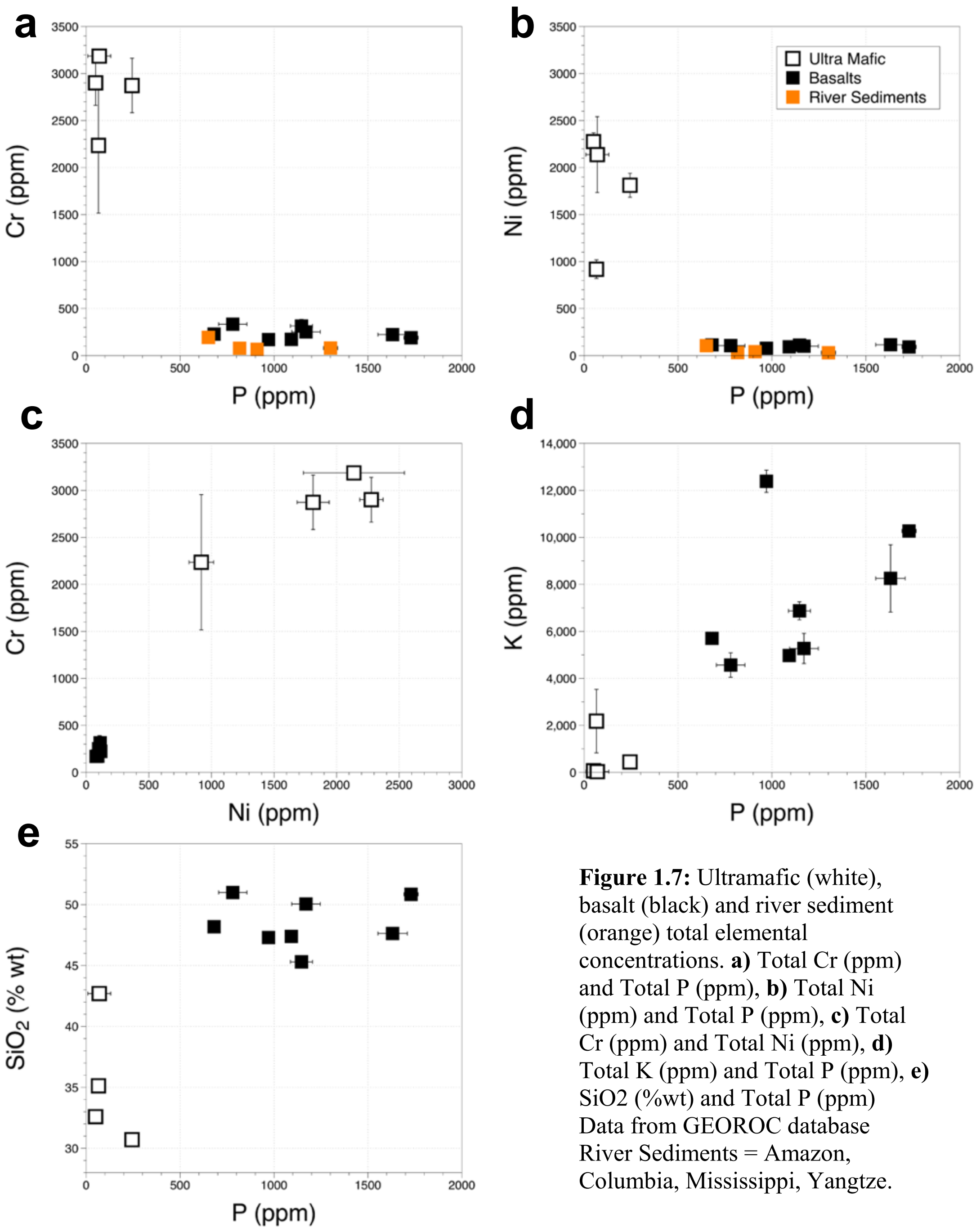


Figure 1.7: Ultramafic (white), basalt (black) and river sediment (orange) total elemental concentrations. **a)** Total Cr (ppm) and Total P (ppm), **b)** Total Ni (ppm) and Total P (ppm), **c)** Total Cr (ppm) and Total Ni (ppm), **d)** Total K (ppm) and Total P (ppm), **e)** SiO2 (%wt) and Total P (ppm) Data from GEOROC database River Sediments = Amazon, Columbia, Mississippi, Yangtze.

However, research comparing published chemical analyses from the GEOROC database, specifically looking into the prevalence of olivine, a fast weathering, mineral showed that the most likely source were igneous basic ultramafic (<45 %wt SiO_2); peridotites: dunite, harzburgite, lherzolite and wehrlite (Beerling et al. 2018a). The weathering of olivine on agricultural land is expected to be even more efficient than that of wollastonite, with a CO_2-capture efficiency of 80-90 % for the mass applied (Renforth 2012). Ultramafic rocks also contain high concentrations of chromium (Cr) and nickel (Ni) and are very low in P and K content, see Figure 1.7. The serpentine soils that develop on ultramafic bedrock have low nutrient content and are easily eroded, and the vegetation that develops is adapted to these conditions and usually endemic to the region such as the forests surrounding Mt Kinabalu in Borneo (Galey et al. 2017).

Conversely, igneous continental flood and convergent margin basalts (>45 % SiO_2) have much lower concentrations of Ni and Cr, but significantly higher concentrations of P, K and SiO_2, indicating their potential as a crop fertiliser (Schuiling and Krijgsman 2006; Mohammed et al. 2014; Noordin et al. 2017). The application of crushed basalt has been found to release essential plant elements and improve soils by increasing SOC and water holding capacity, thus enabling crop yield production potentials to be met (Gillman 1980; Gillman, Burkett, and Coventry 2001; Nunes, Kautzmann, and Oliveira 2014; Priyono and Gilkes 2008b; Stockmann et al. 2008). However, carbon capture by crushed flood basalts is less effective, achieving only 0.3 t CO_2 per ton of rock dissolved (Renforth 2012). Application rates of 20 T ha^{-1} were the most successful, however these rates are higher than what is practical for farmers where liming rates rarely exceed 10 T hec^{-1} (Borken and Brumme 1997; Brumme and Beese 1992). Milling the rock into smaller particles (< 200 μm), increases available reaction surface area and thus the rate of weathering reactions, lowering necessary application rates (Priyono and Gilkes 2008b). However, the energy cost associated with mining and grinding potentially reduces the net carbon drawdown by 10 - 30 %, resulting in actual costs at \$52 – \$480 t CO_2 (Moosdorf, Renforth, and Hartmann 2014; Renforth 2012). The associated costs from grinding and transporting basalts limit their potential as a sustainable solution. This suggests that further research into alternative sources of crushed rock, utilising natural sediment ‘factories’ such as rivers or glaciers could provide a novel solution.

Thus far, this literature review has discussed the qualities determining the potential of crushed rock application for sustainable agriculture. These key features for success in line with UN SDGs are as follows: 1) Small particle size, large surface area, 2) Rich in silicates, 3) Crystal structure susceptible to weathering, 4) High in macro and micronutrients, low in bio-labile toxic metals, 5) Low cost, both economical and environmental, 6) Available in areas with need or already present organic farming markets and knowledge. The following part of this literature review will assess an alternative source of crushed rock against these qualities, glacial sediments.

1.2.3.1 Glacial flour

Glacial flour has potential as a novel source of crushed rock for sustainable agriculture because of four key features; glaciers and icesheets are powerful erosive agents, combining intense physical and chemical erosion, key geological features, and high sediment exports, whilst occurring in a variety of globally significant locations. These factors are discussed below.

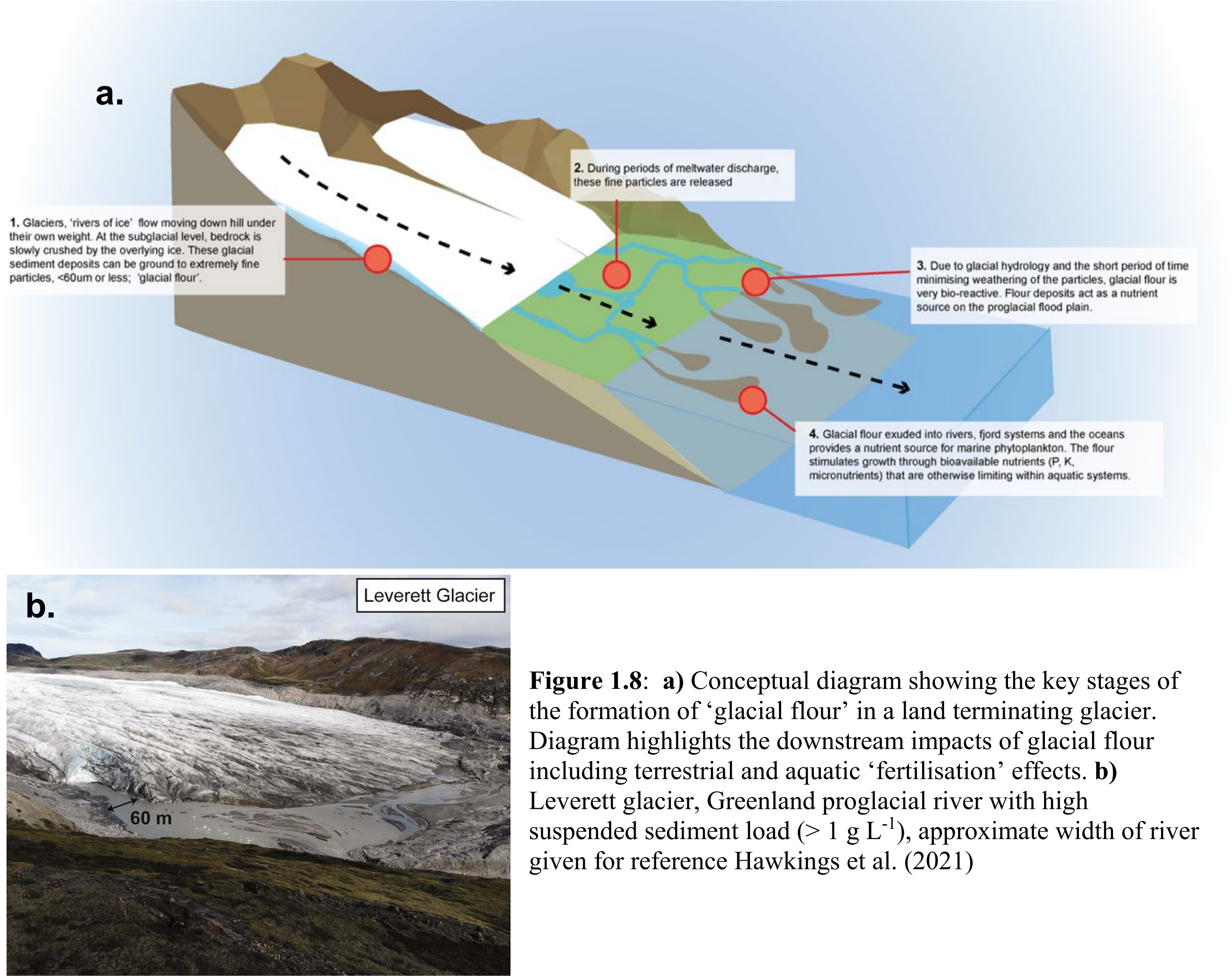


Figure 1.8: **a)** Conceptual diagram showing the key stages of the formation of 'glacial flour' in a land terminating glacier. Diagram highlights the downstream impacts of glacial flour including terrestrial and aquatic 'fertilisation' effects. **b)** Leverett glacier, Greenland proglacial river with high suspended sediment load (> 1 g L^{-1}), approximate width of river given for reference Hawkings et al. (2021)

First, glaciers and ice sheets are large erosive agents, fracturing and grinding bedrock into large surface area, highly reactive silt sized (< 66 μm) particles, 'glacial flour',) see Figure 1.8A, B (Gurnell and Clark 1987; Brown, Tranter, and Sharp 1996b). This particle size is far less than the recommended minimum particle size used in crushed rock agriculture (150 μm), alleviating the need for high-energy, costly milling processes (Priyono and Gilkes 2008a).

Second, glacial flour can be associated with important geological factors required for agriculture involving the use of crushed rock. Past research, focussed on glaciers overlying silicate bedrock (e.g. Leverett glacier, Greenland), has shown that glaciers and ice sheets export large quantities of nutrients, N, P, C, Fe and Si in meltwater and the particulate bound fraction of nutrient loads is dominant for rock bound nutrients (Si > 99 %, P ~ 80 %) shown to impact global ocean and terrestrial biogeochemical cycles (Bhatia et al. 2013; Death et al. 2014; Hood et al. 2015; Hood et al. 2009; Hawkings et al. 2015a; Lawson et al. 2014; Wadham et al. 2016; Raiswell and Canfield 2012; Schroth et al. 2014; Föllmi et al. 2009; Hendry et al. 2019). Furthermore, past research has determined that glacial meltwaters act as a CO_2 drawdown mechanism, dependent on rock type (Sharp et al. 1995). This evidence suggests that glacial sourced crushed silicate bedrock may have potential in enhanced weathering application.

Third, glacial flour transported in runoff as suspended material can be exported in vast quantities, providing a sustainable and consistent supply (Greenland, > 1 g L^{-1}, Himalayas < 1 g L^{-1}) (Cowton et al. 2012; Singh et al. 2015). Furthermore, research within subglacial hydrology has shown that glacial flour is flushed out annually via a series of fast, efficient channelised systems (Chandler et al. 2013; Hubbard and Nienow 1997). Although some subglacial sediment water stores have longer residence times and can be subjected to biological weathering reactions, annual sediment flushing in spring provides a large quantity of relatively unweathered 'fresh' finely crushed bedrock (Mikucki et al. 2016; Mitchell et al. 2013; Lamarche-Gagnon et al. 2019; Macdonald et al. 2018). The unique regime of glacial systems results in a large supply of unweathered rock, an important feature for supplying glacial flour for agriculture.

Finally, glaciers are globally significant sources of sediments, occurring in almost every continent in high-latitude and high-altitude regions, see Figure 1.9. For glacial flour to be an effective sustainable solution it needs to be accessible and there needs to be a local demand. Against this backdrop, regions such as the Himalaya are potential sites for glacial flour based agroecology. Often referred to as the third pole, Himalayan glaciers cover an area of 4.2 million km^2, acting as the frozen water towers at the source of the 10 major river basins of Asia (Wester et al. 2019). These river basins are essential, directly supporting 240 million people's lives and livelihoods, while 1.9 billion rely on them for water, food and energy (Rasul 2014). Furthermore, there is a need for sustainable soil treatment solutions and a growing demand in organic / agroecological farming across the region within low input smallholder farms (Khattri and Pandey 2021; Wester et al. 2019). However, despite past research indicating positive features for glacial flour as a soil treatment, significant knowledge gaps remain.

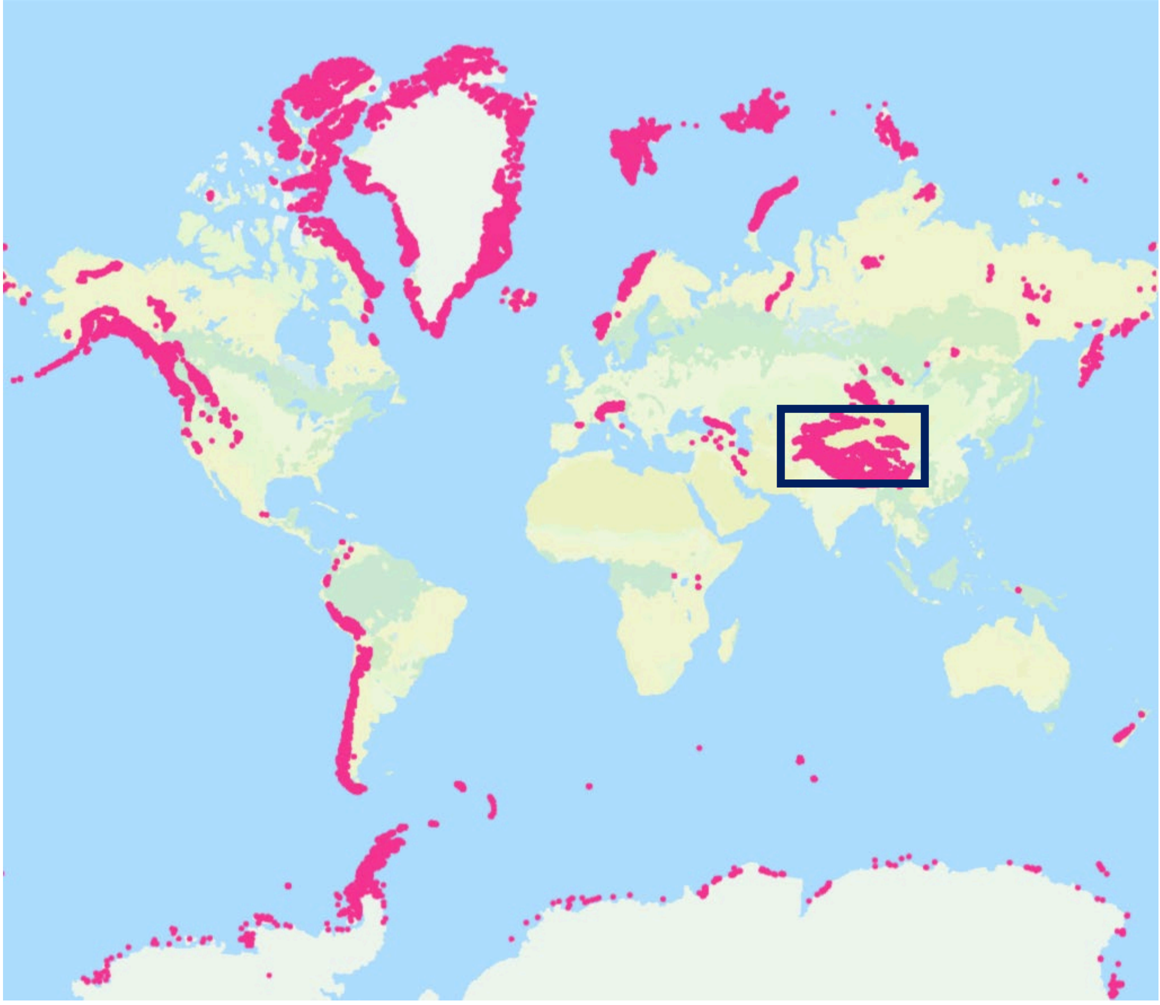


Figure 1.9: Global glaciers – glaciers are found on nearly every continent but predominantly in high latitude and high-altitude regions. At this scale glaciers are exaggerated. Black rectangle indicates the Himalayas. *Randolph Glacier Inventory, GLIMS.*

Past biogeochemical research has focused upon large icesheets such as Greenland and Antarctica, with little biogeochemical data covering low-latitude glaciers. Furthermore, past research into glacial flour bound nutrients has quantified important ocean biogeochemical nutrients (N, P, C, Fe and Si), but has failed to address important terrestrial nutrients key to plant growth (P, K, S, Ca, Mg, Fe, Mn). Decreasing these knowledge gaps between marine and terrestrial, high latitude and low latitude glacial biogeochemistry will not only advance glacial biogeochemical research, but also allow for the determination of glacial flours potential within agriculture. Although recent research has investigated the potential of Greenlandic granitic glacial deposits for farming, there has been no experimental enquiry into freshly sourced glacial flour from alternative bedrocks, such as basalts, with a more suitable dissolution potential (Sukstorf, Bennike, and Elberling 2020). Finally, there has been no investigation into the impact glacial flour treated soils have upon crop trace element concentrations and potential effects on human nutrition.

1.2.4. Summary and research gaps

Despite great progress in the understanding and development of crushed rock for agriculture over the past few decades, for it to be effective there is a need to reduce economic and environmental costs by determining a sustainable source of finely crushed rock. Sustainable agricultural methods dominate small-holder, low input farming systems in large regions in proximity to regions with substantial glacial cover, such as the Himalayas. Only by studying glacial flours with a variety of different bedrocks and their effect upon crops in a controlled laboratory investigation, will we begin to determine glacial flours potential.

Recent research has identified glaciers as a significant nutrient source to downstream ecosystems. The impact of these nutrients has been of notable interest in productive fjord and marine ecosystems; however, studies have been focused upon high latitude regions such as Greenland and Antarctica. Data for glaciers outside of this region is lacking. Performing a global investigation into glacial particulate nutrients will allow for comparisons between bedrock and glacial cover (Chapter 3). The speciation of nutrients bound to particulate fraction will also provide unique knowledge about biogeochemical fluxes from glacial systems. Producing a robust dataset on glacial flour nutrients will also support the investigation into the potential of glacial flour as an agricultural strategy.

Only one study has investigated the potential of glacial flour as a source of nutrients for crops (Sukstorf, Bennike, and Elberling 2020). However, the sediments used in this investigation were highly weathered glacio-fluvial lake deposits, collected from a core sample, no study to date has investigated the potential of freshly deposited glacial flour from riverbanks as a novel source of crushed rock with agroecological systems. Past crushed rock laboratory experiments have grown a variety of crops, however significant positive yield effects were seen on legume crops. A robust investigation into the impact of glacial flour on legume growth yield would provide an invaluable first step in assessing glacial flour within agriculture (Chapter 4). This growth experiment would provide the first ever plant growth investigating into glacial flour and plants. This will not only be the first crop growth experiment using 'fresh' glacial flour but will also advance the crushed rock research field.

The growth experiment and assessment of the full suite of macro and micronutrients may also inform us further of the potential crushed rock may have as a source of not only macro but micronutrients. A concern within crushed rock research is the accumulation of toxic metals in crops, therefore it is necessary to also establish crop micronutrient and metal content and uptake. Therefore, the crop investigation performed on legumes will then provide the first steps to assess elemental uptake from glacial flour sediments (Chapter 5). This will determine potential beneficial and toxic enrichment following glacial flour application.

Addressing these knowledge gaps, whilst undertaking a novel crop growth investigation form the research questions of this thesis. The unique research questions posed in this thesis span multiple fields of research. Through improving knowledge of glacial biogeochemistry, we also aim to advance the field of agroecology and determine the potential of glacial flour as a sustainable soil treatment for low-input farmers of the Global South.

1.3 Aims and Objectives

1.3.1 Primary research aim

Determine the importance of glacial flour as a source of nutrients and trace elements to assess its potential as a novel soil treatment for agriculture.

1.3.2 Objective 1 (Chapter 3)

Identify how the nutrient content (macro and micronutrients) and speciation of glacial flour varies globally, evaluating the importance of bedrock.

Hypothesis 1a: Nutrient content and speciation is determined by bedrock geology and mineralogy

Hypothesis 1b: Glacial flour contains beneficial nutrients for crushed rock agriculture

Hypothesis 1c: Glacial flour contains toxic trace elements with potential to be mobilised in soils

This objective will be achieved by collecting and analysing global glacial flours from large ice sheets in high latitudes and mountain glaciers globally. This will be the first synthesis of glacial particulate nutrients and metal content, especially in under-studied low latitude mountain glaciers. The results and discussion of this objective are presented in Chapter 3.

1.3.3 Objective 2 (Chapter 4)

Perform an exploratory novel crop growth investigation to assess the effect glacial flour has upon the yield, health and nutritional value of leguminous crops

Hypothesis 2a: Glacial flour acts as a source of macro and micronutrients enhancing crop yields

Hypothesis 2b: Glacial flour improves plant health and legume-rhizobia relationship

Hypothesis 2c: Glacial flour has potential to enrich crops with beneficial nutrients for human diets

To evaluate glacial flour as a novel soil treatment, the primary objective of Chapter 4, is delivered via the first laboratory crop growth trials using glacial flour. Photosynthetic capacity measurements will be used as an indicator of plant health, alongside biomass, crop yield and nodule counts. The used of a legume crop, soybeans, is of commercial interest due to being a key crop in low-latitude sub-tropical / tropical regions. For the first time, this thesis will present glacial flour crop treated data compared with a control and chemical fertiliser experiments. The investigation presented in Chapter 4 is a novel proof of concept, starting to address some of the key issues of crop production in the Global South.

1.3.4 Objective 3 (Chapter 5)

To evaluate the toxic bioaccumulation and beneficial biofortification of trace elements in glacial flour treated legumes.

Hypothesis 3a: Glacial flour has the potential to enrich soybeans in macronutrients and trace elements

Hypothesis 3b: The level of enrichment in the crop is dependent on glacial flour application rate

Hypothesis 3c: Bedrock source of glacial flour regulates crop element concentration through chemical weathering in experimental soils

Hypothesis 3d: Glacial flour application does not pose a risk to human health via either acute or chronic toxicity

A thorough evaluation of the elemental concentration of the soybean crop yield grown during the experiments presented in Chapter 4 will meet objective 3. Trace element extractions on the soybeans will be performed providing a full dataset on soybean elemental uptake following glacial flour application. This will be the first agricultural investigation to fully assess trace element uptake following a natural crushed rock treatment, expanding current knowledge within the field. Determining trace element uptake within the glacial flour treated soybeans will also highlight any potential toxicity risks for downstream communities.

Chapter 2: Field Sites and Methodology

2.1 Field Sites

2.1.1 Global glaciers

This thesis presents data from 11 glaciers across varied global glaciated regions (Figure 2.1). To develop knowledge of glacial sediment-bound nutrients, spatial coverage was achieved by accessing previously collected and new samples. Glaciers were chosen based on differing bedrock geology (igneous, metamorphic, and sedimentary), mineralogy (for example the differing dissolution rate between granite and basalts), past data availability and accessibility (Figure 2.1). Land-terminating glaciers have potential to act as 'sediment factories', releasing high quantities of nutrient-rich suspended sediment (up to 1 g L^{-1}), 'glacial flour' (Cowton et al. 2012). Glacial flour released from glaciers has potential to be accessible and all but the Greenlandic glaciers studied are located near areas of potential agricultural demand (Brown, Tranter, and Sharp 1996b). Sampling has focused on glaciers where the subglacial meltwater channel exits through a single portal creating one proglacial river or ice-marginal lake. The presence of a single direct source of subglacial sediment reduces sampling complications ensuring minimal mixing with other potential sediment inputs. However, samples from Steffen glacier were an exception, and are taken downstream from a large proglacial lake with multiple inputs. To test the hypothesis that glacial flour has the potential to improve crop yield, focused crop yield investigations were performed using glacial flour from two model glaciers: Sólheimajökull glacier, Iceland and Chhota Shigri glacier, HKH India. Reasons for this are detailed in section 2.1.2 and 2.1.3.

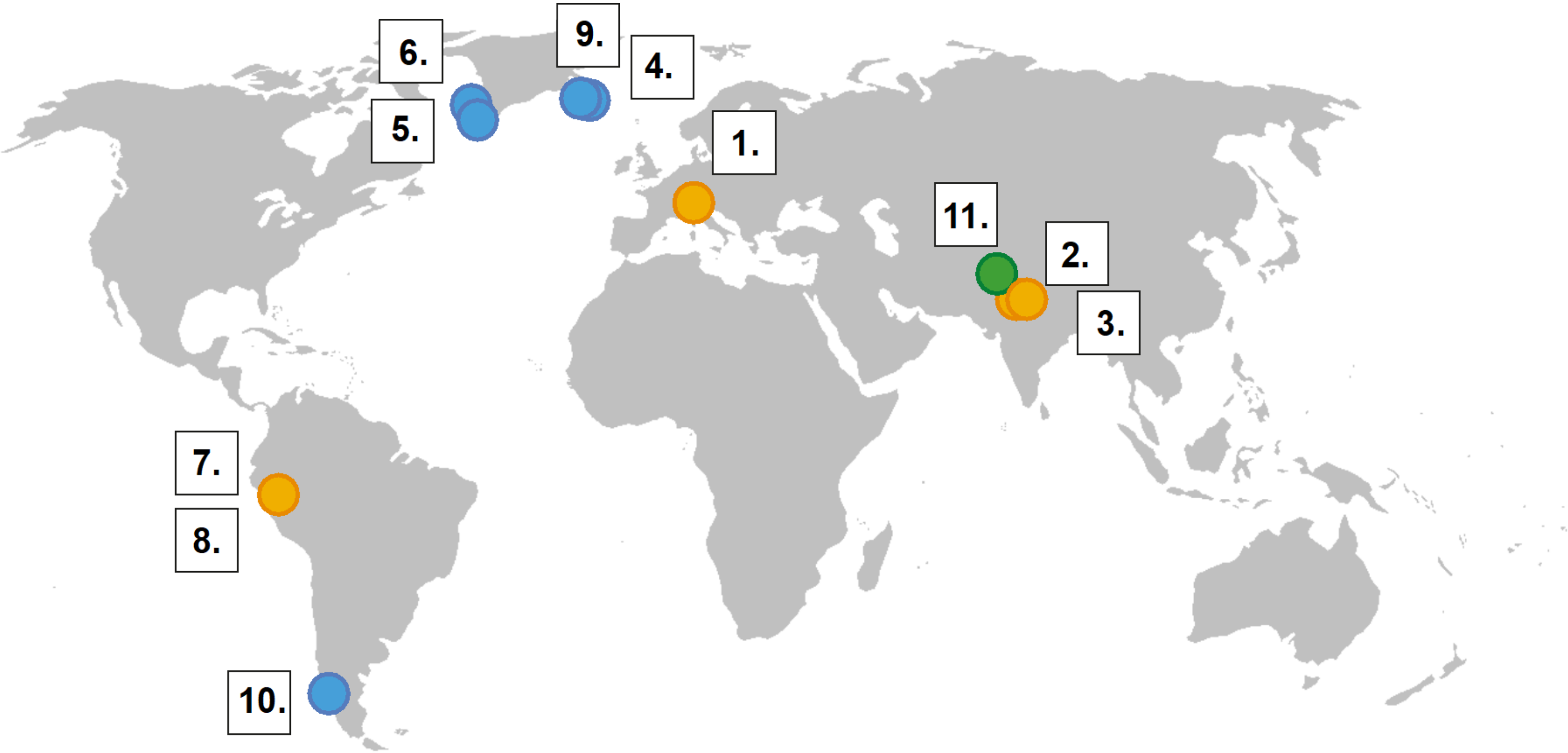


Table 2.1: Global Glacier sampling locations and geology

	Glacier	Location	Geology	Bedrock	Catchment Area (km^2)	Glacial cover (%)	Reference
1	Haut Glacier d'Arolla	Swiss Alps	Schistose granite, some gneiss, greenschist, amphibolite and gabbro intrusion, trace carbonates	Met-Sed	11.7	54	Tranter, Sharp et al. (2002)
2	Bara Shigri	Hindu Kush Himalaya (India)	Schistose granite, fine grained biotite schist, black slates and phyllite	Met-Sed	272	48	Singh and Ramanathan (2015)
3	Chhota Shigri	Hindu Kush Himalaya (India)	Gneiss, some granite, chalcopyrite, some veins of black slates and phyllite	Met-Sed	36.7	43	Singh, Ramanathan et al. (2015)
4	Falljökull	S Iceland	Basalts, icelandite, breccias, rhyolite	Igneous	26.5	68	MacDonald, Black et al. (2016)
5	Kiattuut Sermiat	SW Greenland	Granite, small complexes of diorite, pyroxene, biotite monozonite and basaltic intrusions	Igneous	36	98	Henriksen, Higgins et al. (2009), Hawkings, Wadham et al. (2016)
6	Leverett	SW Greenland	Ancient crystalline granite / gneiss	Igneous	600	100	Henriksen, Higgins et al. (2009), Hawkings, Wadham et al. (2016)
7	Pastoruri*	Cordillera Blanca, Andes	Pyrite schists, phyllite and pyrite bearing quartzite, and a central granodiorite tonalite batholith, Sandstones, lutites	Met-Sed	0.76	54	Fortner, Mark et al. (2011), Santofimia, López-Pamo et al. (2017)
8	Shallap*	Cordillera Blanca, Andes	Pyrite schists, phyllite and pyrite bearing quartzite, and a central granodiorite tonalite batholith, Sandstones, lutites	Met-Sed	12.3	31	Fortner, Mark et al. (2011), Schauwecker, Rohrer et al. (2014)
9	Sólheimajökull	S Iceland	Basalts, breccias, rhyolite, palagonite	Igneous	78	56	Wynn, Morrell et al. (2015)
10	Steffen	Northern Patagonian Ice cap	Granite, hornblende-biotite, granodiorite, tonalite, leucogranite	Igneous	671	71	Pryer, Hawkings et al. (2020), Pankhurst, Weaver et al. (1999)
11	Tirich Mir	Hindu Kush Himalaya (Pakistan)	Granite, slate, siltstones, quartzites, ferrogenous limestones and calcareous schists	Igneous-Sed	266	25	Heft (1986)

Figure 2.1, Table 2.1: Global glacier sampling locations, bedrock type, geology, glacial catchment area and glacial cover. Colours represent bedrock type. Yellow = Met / Sed mixed, Blue = Igneous, Green = Igneous-Sedimentary.

2.1.2 Sólheimajökull Glacier, Iceland

Sólheimajökull (63.4° N, 19.4° W) is a land terminating glacier in SW Iceland, approximately 165 km SE of capital city of Reykjavík (Dugmore 1989). The glacier is 11 km long by 1 – 2 km wide (Carswell 1983). It is a glacial outlet of the southern part of the Myrdalsjökull ice cap, lying above the Katla volcanic system see Figure 2.2a (Wynn et al. 2015). The volcanic system consists of the active central Katla volcano and fissure swarm (Duller et al. 2008; Sturkell et al. 2010). It is a mid-sized catchment with an area of approximately 78 km^2 (Guan et al. 2015). The glacier descends from 1350 to 100 m a.s.l. where it terminates as a 1.5 km wide glacier tongue. Here, the central portion of the snout terminates in an ice-marginal lake, the rest ends on proglacial sediment deposits, see Figure 2.2c (Björnsson, Pálsson, and Gudmundsson 2000). Average summer and winter discharge at Sólheimajökull are estimated to be 50 m^3 s^{-1} and 10 m^3 s^{-1} respectively (Lawler, McGregor, and Phillips 2003). Glacial meltwater from Sólheimajökull drains southwards via a 1 km long subglacial tunnel (Burns et al. 2018). Downstream from the ice-marginal lake outlet, meltwater

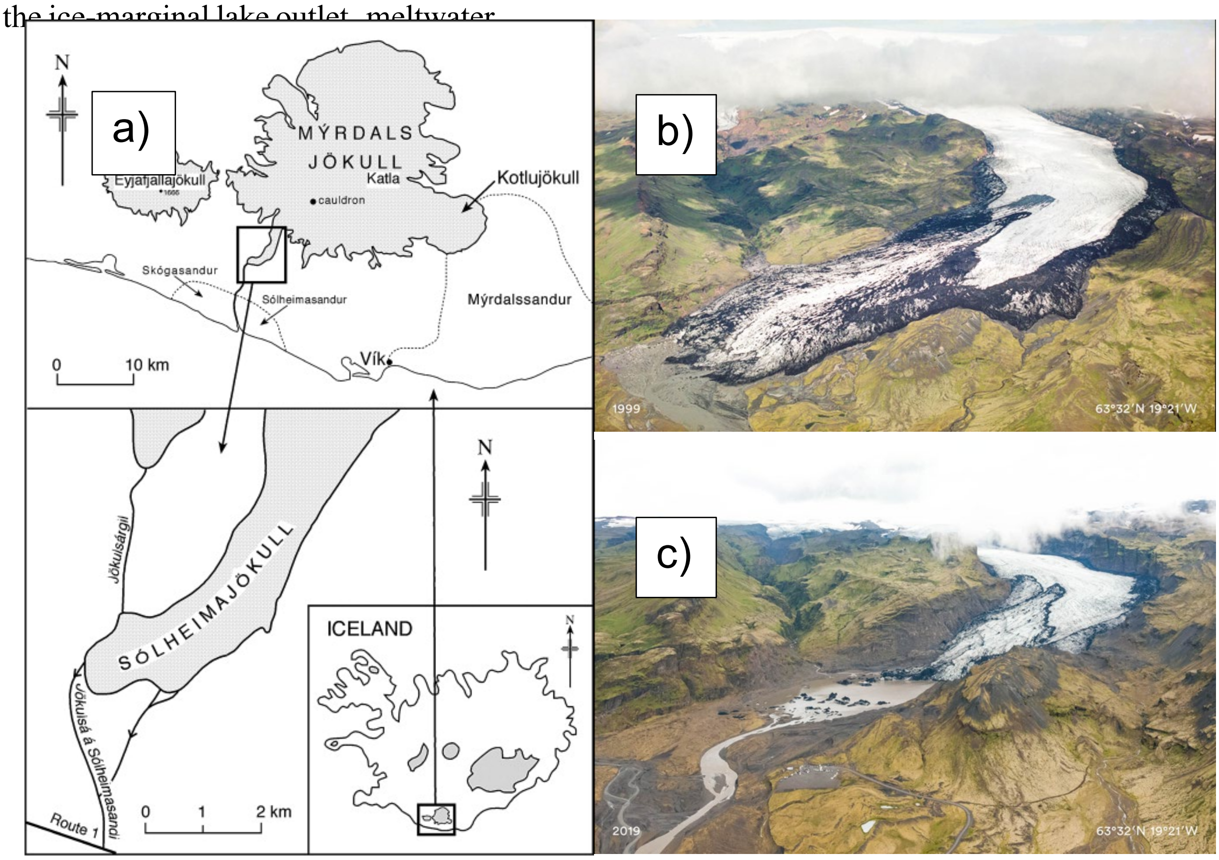


Figure 2.2: a) Map of Sólheimajökull glacier, showing location in SW Iceland and upon Myrdalsjökull ice cap. Also shows tributaries. (Russell et al. 2010) **b)** Sólheimajökull in 1999. **c)** Sólheimajökull in 2019. Both b and c aerial photos used with permission from www.glacier.is

joins two other flow sources; 1) Jökulsár gilsojökull, an outlet glacier 3 km to the north of Sólheimajökull and 2) the river Fjallgilsá, flowing into the Jökulsá approximately 2 km downstream towards the Atlantic Ocean within the river Jökulsá á Sól-heimasandi (also known as Fúlilækur) (Burns et al. 2018; Guan et al. 2015). Sediments transported via the subglacial meltwater channel are deposited on the banks of the ice-marginal lake, prior to the confluence with the Jökulsár gilsojökull glacial stream. This isolated source reduces complications with sampling. Sólheimajökull glacier has historically been prone to large subglacial outburst drainage events; 'jökulhlaups' (Russell et al. 2003).

Intense discharge events, jökulhlaups, are possible because volcanically generated geothermal ice-melt due to Sólheimajökull catchment reaching into the SW rim of the Katla subglacial caldera (Björnsson, Pálsson, and Gudmundsson 2000; Larsen 2010; Larsen et al. 2001). During large jökulhlaup events discharge can reach up to 4.4 x 10^3 m^3 s^{-1}, although permeable outwash plains comprising of braided channels are effective in damping peak discharge impacts, jökulhlaups can generate large geomorphological landscape changes (Russell et al. 2010; Russell et al. 2003). During the 1999 jökulhlaup, significant quantities of sediment laden floodwaters (30 % clay, 85 % silt or finer) as well as a large (> 200 m) coarse ice-proximal boulder bar was deposited (Russell et al. 2003).

Although there is the potential for jökulhlaups to generate large sediment deposition events, Sólheimajökull meltwater transports high quantities of suspended sediment over a year, giving typical suspended sediment concentrations of 500 mg l^{-1} and suspended sediment loads of 7.6 kg s^{-1} (Lawler, McGregor, and Phillips 2003). The consistent quantity of subglacial sediments, glacial flour, released from Sólheimajökull is one reason for its inclusion in the crop yield investigation. However, it is not only the availability of sediment but also the geochemical features of the sediment itself that point towards Sólheimajökull flour as an ideal rock type for agricultural application.

Past research has focussed upon the geological formation and volcanic activity of Iceland (Saemundsson 1979). Iceland is a young volcanic island, forming approximately 16 - 18 Mya (Vink 1984). It is located on top of a mantle plume and at the junction of two submarine ridges, the Mid-Atlantic Ridge, an active spreading boundary and the Greenland-Scotland transverse ridge at the plate boundary between the diverging North American and Eurasian plates (Pálmason and Saemundsson 1974; Pálmason et al. 1979). Driven by long-standing geological research interests, Icelandic geology has been mapped, although some gaps remain beneath glacial cover (see Figure 2.3). The bedrock geology underlying the Sólheimajökull catchment is dominated by recent volcanic basalt lava, which is classified into three distinct groups; tholeiites, transitional alkali basalts and alkali olivine basalts (Jakobsson 1972; Saemundsson 1979; Raiswell and Thomas 1984). Basalts have been highlighted as the 'ideal' bed rock type for agricultural application (Köhler, Hartmann, and Wolf-Gladrow 2010; Beerling et al. 2018b).

Sólheimajökull flour has specific geochemical qualities that enable it to act as a model system for the application of glacial flour to agricultural soils. First, the basalt bedrock of Sólheimajökull is generally younger than 0.7 M years, with some lavas younger than 10,000 years, having formed post-glaciation and contains an array of nutrients (Bamlett and Potter 1988). These young basalts typically contain varying quantities of elements such as K, P, Fe, Mn, Co, Ni, Mg, Ca as well as an array of rare earth elements (Sigmarsson and Steinthórsson 2007; Wood 1978; Larsen, Dugmore, and Newton 1999). Second, the basalts are expected to have a fast dissolution rate, suggested by the high quantities of olivine and other loosely bound silicate rocks (Gislason and Arnórsson 1993; Georg et al. 2007). This relatively fast nutrient release could provide the crop and microbiota with a new source of primary macro and micronutrients unavailable within poor soils (Hartmann, West, Renforth, Kohler, et al. 2013).

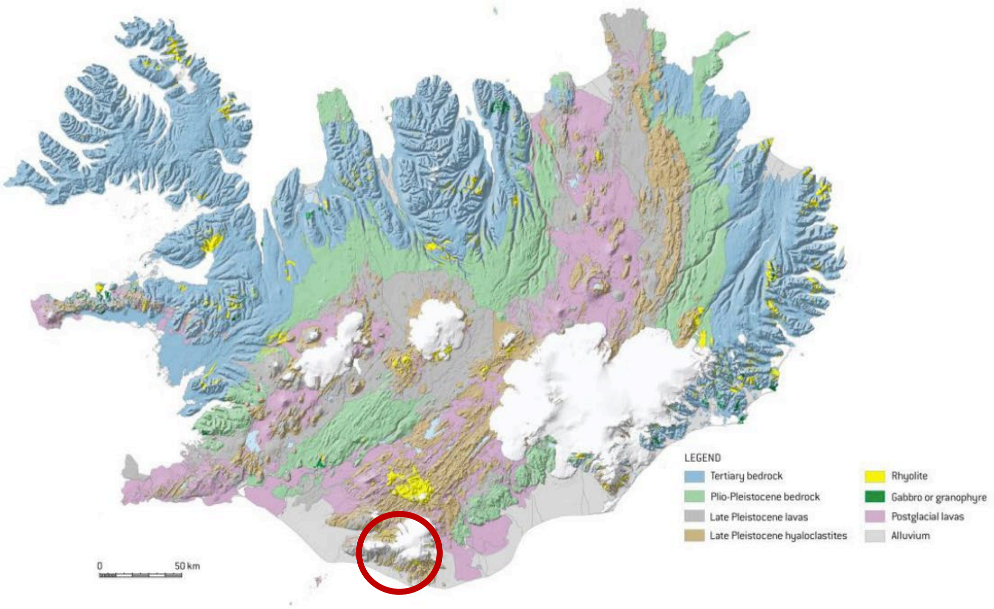


Figure 2.3: Geological map of Iceland, Red circle marks location of Myrdalsjökull ice cap and Sólheimajökull outlet glacier. Rock types are predominantly Late Pleistocene hyaloclastites, rhyolites and post glacial lavas. Large alluvium deposits also span the South coast. Iceland 1:1.000.000. Icelandic Institute of Natural History. Adapted from Snæbjörnsdóttir et al. (2014).

The array of nutrients held within Icelandic basalts; alongside prospective dissolution rates imply that glacial flour sourced from Sólheimajökull is worthy of further investigation. However, it is unknown how beneficial and potentially toxic metals, such as Fe, Mo, Cr and Ni present in Sólheimajökull bedrock may impact crop growth and nutritional value.

Current research on Icelandic glaciers focuses on developing innovative geo-engineering solutions and improving hazard risk and resilience against the backdrop of a changing climate (Gudmundsson et al. 2008). New technology linking the high reactivity and weathering potential of Icelandic basalts to CO_2 drawdown has been successful (Clark et al. 2020). It has been shown that Icelandic basalt bedrocks can be employed in mineral carbonation, a process in which CO_2, other acid gases and H_2O are injected into deep geological reservoirs to precipitate with Ca and Mg-silicate rocks for long term carbon capture and storage (Matter et al. 2009; Clark et al. 2020; Snæbjörnsdóttir et al. 2020). Furthermore, this recent research supports Icelandic glacial flour's potential as a geo-engineering enhanced weathering strategy, potentially drawing down CO_2 when applied to agricultural land. For glacial flour to be accessible, there must be flushing of subglacial meltwaters and glacial erosion. Glaciers in Iceland are under threat from climate warming which have the potential to affect glacial flour supplies (Sigurđsson, Jónsson, and Jóhannesson 2007).

Approximately 11 % of Iceland is covered by glaciers (Bjornsson 1978). It is expected that with changing climate, Icelandic ice caps will lose 25 – 35 % of their present volume in the next 50 years, when it is likely glacial meltwater runoff will peak aand then decline to present-day values 100 years from now (Björnsson and Pálsson 2008). The disappearance of the Icelandic glacier, Okjökull hit the mainstream news headlines in 2019. 'Ok' lost status as a glacier in 2014 and researchers gathered in Borgarfjördur, Iceland to memorialise Okjökull with a monument and plaque "A letter to the future" (Fried 2020). The large retreat seen at Sólheimajökull is typical of warming Icelandic glaciers, between 1996 and 2010 Sólheimajökull terminus has retreated on average 40 m yr^{-1}, see comparison aerial images in Figure 2.2b,c (Staines et al. 2015; Sigurđsson, Jónsson, and Jóhannesson 2007). Despite the expected rapid retreatment of Sólheimajökull, heavy amounts of precipitation are predicted to ensure fluvial sediment transport of glaciogenic sediments long after complete deglaciation (Björnsson and Pálsson 2008; Crochet et al. 2007). This implies that the Sólheimajökull catchment may provide a long-term source of rock flour if the glacier was to disappear, however studies into the weathering of glacial flour are required.

This thesis hypothesises that glacial flour sourced from Sólheimajökull will act as a model flour type for agricultural application. In summary, the key attributes of Sólheimajökull flour are as follow; firstly, Sólheimajökull glacier produces large quantities of subglacial sediments every year and will continue to do so for a minimum of 100 years (Staines et al. 2015). The availability of glacial flour is a positive feature. Secondly, Sólheimajökull flour consists of nutrient rich basalts with high weathering potential and therefore prospective nutrient release and enhanced weathering application (Beerling et al. 2018b; Jakobsson 1972). Nonetheless, there is an unknown regarding potential heavy metals and the impact this may have upon crops in the short and long term (Larsen, Dugmore, and Newton 1999). Finally, Sólheimajökull is very accessible, minimising fieldwork constraints and ensuring sample collection.

2.1.3 Chhota Shigri glacier, Hindu-Kush Himalaya, India

Adoption of glacial flour farming requires both access to glacial flour and agroecological farming networks likely to up-take the strategy. One key application region is the Himalaya; regarded as the 'Third Pole', the Himalaya has the largest concentration of glaciers outside the polar region that are heavily relied upon for water, energy, agriculture by the 2 billion population downstream (Wester et al. 2019). Against this backdrop, establishing knowledge around whether glacial flour from these regions acts as a successful soil treatment will be decisive in determining its full potential. Himalayan glaciers tend to be understudied, with research in the region heavily reliant on remote sensing (Berthier et al. 2007). Field measurements at high altitude Himalayan glaciers are still challenging compared with their low latitude counterparts, however, Chhota Shigri glacier has been studied as a representative Himalayan glacier for over 15 years (Shea et al. 2015; Germann et al. 2006; Ramanathan 2011). This thesis will use Chhota Shigri glacial flour as a representative flour from the NW Himalayas with similar bedrock.

Chhota Shigri glacier (32.2° N, 77.5° E) is a typical Himalayan low latitude glacier located in the Chandra-Bhaga river basin of Lahaul and Spiti valley, Pir Panjal range, North Western Himalaya, see Figure 2.4 (Azam et al. 2012). Chhota Shigri is located in the monsoon-arid transition zone and is subjected to two different weather systems: the Indian monsoon during summer (July – September); and the Northern Hemisphere mid-latitude westerlies during winter (January – April) (Singh, Jain, and Kumar 1997; Bookhagen and Burbank 2006; Gardelle, Arnaud, and Berthier 2011). Chhota Shigri is oriented in a N/NW direction, descends from approximately 6260 to 4050 m a.s.l, is approximately 9 km long and covers an area of 16.3 km^2 (Kumar and Dobhal 1997; Wagnon et al. 2007). The lower ablation area of Chhota Shigri (< 4400 m a.s.l) is partly covered by debris, amounting to approximately 3.4% of the total glacier surface area (Wagnon et al. 2007; Azam et al. 2012). The snout opens to a concave portal, which is the only direct subglacial opening from which the glacial stream emerges (Ramanathan 2011).

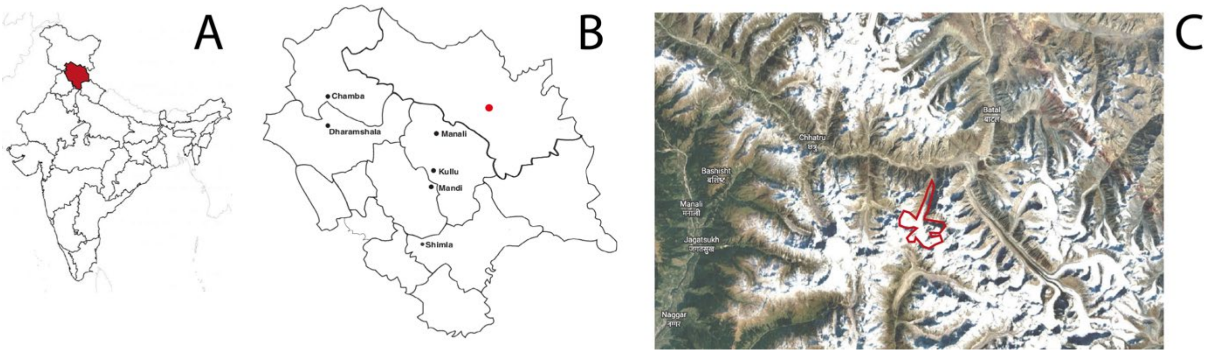


Figure 2.4 – Chhota Shigri location on a variety of scales. **A)** Location of Himachal Pradesh state in NW India. **B)** Red mark indicates location of Chhota Shigri in Himachal Pradesh state, NEE of Manali. **C)** Aerial view of Chhota Shigri (red outline) from Google Earth. Adapted from Azam et al 2012)

The Chhota Shigri pro-glacial stream flows NW, and after 2.5 km it meets the Chandra River, a tributary of the Chenab, which is a tributary of the Indus River (Wagnon et al. 2007). Chhota Shigri discharge measurements have historically only been taken when access is possible, during May – October (Singh, Ramanathan, and Pottakkal 2016b; Singh et al. 2015). Average summer discharge for Chhota Shigri is 3.85 m^3 s^{-1}, at least an order of magnitude lower than Sólheimajökull (Singh, Ramanathan, and Pottakkal 2016b). This is to be expected for a small ‘alpine’ valley glacier compared to an ice cap outlet. Across the 2010 season, the average suspended sediment concentration in the proglacial river was 370 mg L^{-1} and suspended sediment load was 1.86 kg s^{-1} (Singh, Ramanathan, and Pottakkal 2016b; Wagnon et al. 2007). Although Chhota Shigri produces less suspended sediment than Sólheimajökull, there are approximately 9600 glaciers over 40,000 km^2 across the Himalayan region which drain into 8 important Asian rivers, the Indus, Ganges, Brahmaputra, Irrawaddy, Salween, Mekong, Yangtze and the Yellow river (Rasul 2014; Wester et al. 2019). The total sediment yield and the downstream impacts of Himalayan glacial suspended sediment is unknown. Investigating Chhota Shigri suspended sediment nutrients as a proxy for other Himalayan glaciers with similar geology will provide new information on suspended sediment nutrient fluxes in Himalayan rivers.

Chhota Shigri glacier falls in the Central crystalline region of the Pir Panjal range of the Hindu Kush Himalayas (Singh and Ramanathan 2018). The crystalline axis is mostly composed of granites, metamorphites, migmatites and gneisses (Kumar and Dobhal 1997). The geology of underlying bedrock at Chhota Shigri is predominantly metamorphic – igneous and is dominated by Rohtang gneisses (Kumar and Dobhal 1997; Singh et al. 2015). Current understanding following low resolution geological mapping is that 3km upstream from the confluence between the Chhota Shigri proglacial river and the Chandra River at Chhota Dara, the bedrock changes, exposing older Proterozoic granites which are mixed with the Haimanta formation of fine metamorphic-sedimentary grained biotite schists, black slates and phyllite, see Figure 2.5 (Singh, Ramanathan, and Pottakkal 2016b; Singh et al. 2015; Kumar and Dobhal 1997). It is unknown how the change in bedrock impacts the Chandra River geochemistry. However, the gneiss bedrock at Chhota Shigri will create flour with a lower weathering potential than the Sólheimajökull basalts. This gneiss may contain beneficial nutrients, however the nutrient content of these sediments and bedrock is unknown.

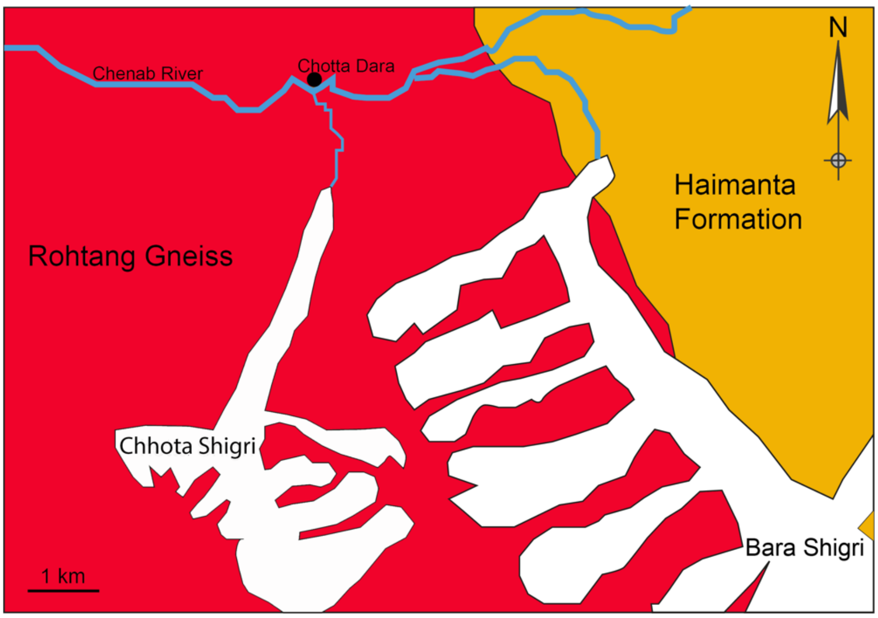


Figure 2.5 – A simplified geological map of Chhota Shigri, red is areas known to be dominated by Rohtang gneiss, yellow is areas known to contain some veins of Haimanta metamorphic-sedimentary bedrock. Based on the map of Singh et al. (2015) and adapted using Google Earth 2020.

Despite many unknowns, Chhota Shigri remains one of the most well studied glaciers in the region (Pandey et al. 2017).

Past research into Chhota Shigri firstly focused on geologically categorising the landscape and then more recently monitoring glacier dynamics, with key focus on glacial retreat (Ramanathan 2011). There is a consensus that the glacier has been retreating for the last 50 years, however there is conflicting data regarding retreat rates, with estimates varying from 25 m yr^{-1} to 53.3 m yr^{-1} (Kulkarni et al. 2007; Gantayat et al. 2017; Ramanathan 2011). These variations appear to reflect differences in methods, from remote sensing to visual observations and glacial mass balance measurements (Azam et al. 2014; Ramanathan 2011; Gantayat et al. 2017; Kulkarni et al. 2007). Complementing research into glacial retreat, research has also begun to elucidate the geochemical characteristics of glacial meltwater to understand the impact upon downstream water quality (Nijampurkar, Sarin, and Rao 1993; Singh, Ramanathan, and Pottakkal 2016b; Singh et al. 2015).

Recent research into meltwater geochemistry at Chhota Shigri has shown that the waters are chemically enriched, showing electrical conductivity values four times higher in subglacial waters (23.2 – 29.0 μScm^{-1}) than supra glacial waters (5.0 – 5.9 μScm^{-1}) (Singh et al. 2015). Since 2008, suspended sediment concentrations, meltwater discharge and sediment load at Chhota Shigri have been monitored (Singh et al. 2015; Singh and Ramanathan 2018). Average Chhota Shigri suspended sediment concentration decreases over the summer months of July – October 2011 – 2014, averaging 883.8 mgL^{-1} in July down to 35.2 mgL^{-1} in October, with peak concentration in July 2011 of 1870 mgL^{-1} and low in October 2013 of 17.9 mgL^{-1} (Singh and Ramanathan 2018). Suspended sediment concentrations in Chhota Shigri waters are highly seasonally variable due to the influences of climate, supraglacial debris and the development of the subglacial drainage system (Pandey, Singh, and Hasnain 1999; Singh et al. 2003). There is the similar seasonal variability in suspended loads, whereby the load considerably decreases across the monitored summer months from average values of 388 $Tday^{-1}$ in July to 6.6 $Tday^{-1}$ in October (Singh and Ramanathan 2018). Despite seasonal monitoring, sediment fluxes are poorly constrained, with sparse measurements only over half of the melt season. This could imply that the annual sediment load from Chhota Shigri is much larger than current estimates.

Chhota Shigri glacial flour is an ideal proxy for Himalayan glaciers. First, Chhota Shigri is well-constrained comparative to other Himalayan glaciers (Ramanathan 2011). Second, the underlying gneiss bedrock is typical of the NW Himalayas and, thus, will act as a measure of potential for glacial flour for agriculture and implications for downstream ecosystems. Third, Chhota Shigri is located where there is a potential market for organic, zero budget farming alternatives (Bharucha, Mitjans, and Pretty 2020). Furthermore, developing knowledge on Himalayan meltwaters geochemistry have the potential for nutrient fluxes to be better understood, such that downstream impacts can be inferred.

2.1.4 Summary of two focused glacial flour sites

The two glacial sites chosen for this body of work differ considerably (Table 2.2). First, Sólheimajökull bedrock is dominated by basalt (igneous), whilst Chhota Shigri bedrock is dominated is gneiss (metamorphic). These two bedrocks have different overall mineralogical composition: basalt is a fine-grained mafic volcanic rock rich in Fe and Mn minerals (e.g. olivine); and gneiss is coarse grained rock, with large interlocking crystals, typically composed of feldspars and is less rich in minerals (Parker 1970). The differences in bedrock type make it possible to assess the potential of glacial flour as a soil treatment, where Sólheimajökull glacial flour might act as the prospective ideal bedrock, whilst Chhota Shigri flour represents flour typical of the Himalaya, a target region for developing agroecological strategies.

Table 2.2: Geophysical parameters of Sólheimajökull and Chhota Shigri. SS = suspended sediment.

	Sólheimajökull, Iceland	Chhota Shigri Hindu Kush Himalaya, India
Geographical position	63.4 N, 19.4 W	32.3 N, 77.7 E
Dominant bedrock	Basalts[1]	Gneiss[2]
Area (approximately km^2)	78	16
Length (approximately km^2)	11	9
Mean Summer Q (m^3 s^{-1})	50*	3.9†
Mean SS concentration (mg L^{-1})	500*	370†
Mean SS load (kg s^{-1})	7.7*	1.9†
References	[1]Carswell (1983) *Wynn et al. (2015)	[2]Kumar and Dobhal (1997) †Singh and Ramanathan (2018)

2.2 Fieldwork

2.2.1 Introduction

The data presented in Chapter 3 of this thesis is largely the result of fieldwork in Iceland, India and Chile. Fieldwork was undertaken at Sólheimajökull and Falljökull, Iceland (2016), Steffen glacier Chile (2017) and Chhota Shigri and Bara Shigri glacier, India Himalayas (2017, 2018). Additionally, to analyse the variation between glacial flours globally, sediment samples are outlined in Table 2.3 and were provided by; Muhammud Rafiq – Tirich Mir, Pakistan (2019), Jemma Wadham – Haut Glacier d'Arolla, Swiss Alps (2017), Jon Hawkings – Leverett and Kiattut Sermiat, Greenland (2018) and Moya MacDonald – Pastoruri and Shallap, Peruvian Andes (2020). Chapter 4 and 5 focused on samples collected from Sólheimajökull glacier, Iceland (2016) and Chhota Shigri glacier, India (2017).

An eight-day trip to Iceland from October 24th, 2016 – November 2nd, 2016, was undertaken. Samples were collected from two glaciers: Sólheimajökull and Falljökull. A sample collection trip to Lambatungnajökull was also carried out, however it was unsuccessful due to the weather conditions. The low water level in meltwater rivers and proglacial lakes at the end of the melt season allowed for easy access to sediment deposits. Following the preliminary fieldwork collecting Icelandic glacier sediment deposit samples, fieldwork was also conducted in Chile (PISCES project) from 3rd July 2017 – 4th August 2017. At Steffen Glacier in Chile, proglacial and suspended sediment samples were collected for this thesis. Further fieldwork was undertaken in 2017 to India 9th – 27th September. The work in the Himalayas was focused at Chhota Shigri glacier. Glacial flour samples were also collected from Bara Shigri glacier and the Chandra River.

Table 2.3: Sampling locations of sediments collected by collaborators

Glacier	Location	Sample coordinates	Date collected	Material type	Provided by
Haut Glacier d'Arolla	Swiss Alps	46.00, 7.49	August 2017	Proglacial stream bank sediment	Jemma Wadham, University of Bristol
Kiattuut Sermiat	SW Greenland	61.21, -45.33	July 2018	Proglacial river bank sediment	Jon Hawkings, University of Pennsylvania
Leverett	SW Greenland	67.07, -50.17	July 2018	Proglacial river bank sediment	Jon Hawkings, University of Pennsylvania
Pastoruri	Cordillera Blanca, Andes	-9.91, -77.18	February 2020	Proglacial lake deposit sediment	Moya MacDonald, University of Bristol
Shallap	Cordillera Blanca, Andes	-9.49, -77.35	February 2020	Proglacial lake deposit sediment	Moya MacDonald, University of Bristol
Tirich Mir	Hindu Kush Himalaya (Pakistan)	36.31, 72.02	September 2019	Proglacial stream bank sediment	Muhammed Rafiq, Quaid-e-Azam University, Islamabad

2.2.2 Glacial flour sampling

Due to the inherent temporal variability of sediment fluxes and deposition regimes between multiple field sites, a standard sampling protocol was developed to ensure comparability of data and to provide the most representative samples. Recently-deposited glacial flour was collected from all sites to ensure comparability. It was assumed that the flour would be most recently deposited at the portal, and thus, avoiding potential downstream transformation. Glacial flour samples provided by other researchers (Arolla, Leverett, Kiattuut Sermiat, Pastoruri, Shallap and Tirich Mir) followed the same sampling procedure as follows.

To avoid contamination, all sampling was performed wearing new, clean nitrile gloves. A plastic trowel was used to collect sediments and was rinsed 3 times in MQ or washed 3 times in site specific proglacial stream water prior to sediment collection. Glacial flour samples were stored in fieldwork fridges if space was available (~ 2 – 4 ºC), otherwise they were kept in a cool box in the shade within 3 hours of sampling. All samples were stored in the refrigerator (~ 2 – 4 ºC) once back in the laboratory.

The five glaciers visited for key glacial flour samples were collected from locations shown in Figure 2.6 as follows. Sólheimajökull flour and Steffen flour were collected immediately in front of the glacier terminus on the banks of the proglacial lake. Chhota Shigri and Bara Shigri flour were collected directly from the banks of the proglacial stream draining from the glacier portal. Field camp set ups for Himalayas and Patagonia are shown in Figure 2.7. Sample site location coordinates where glacial flour was collected by collaborators are outlined in Table 2.2

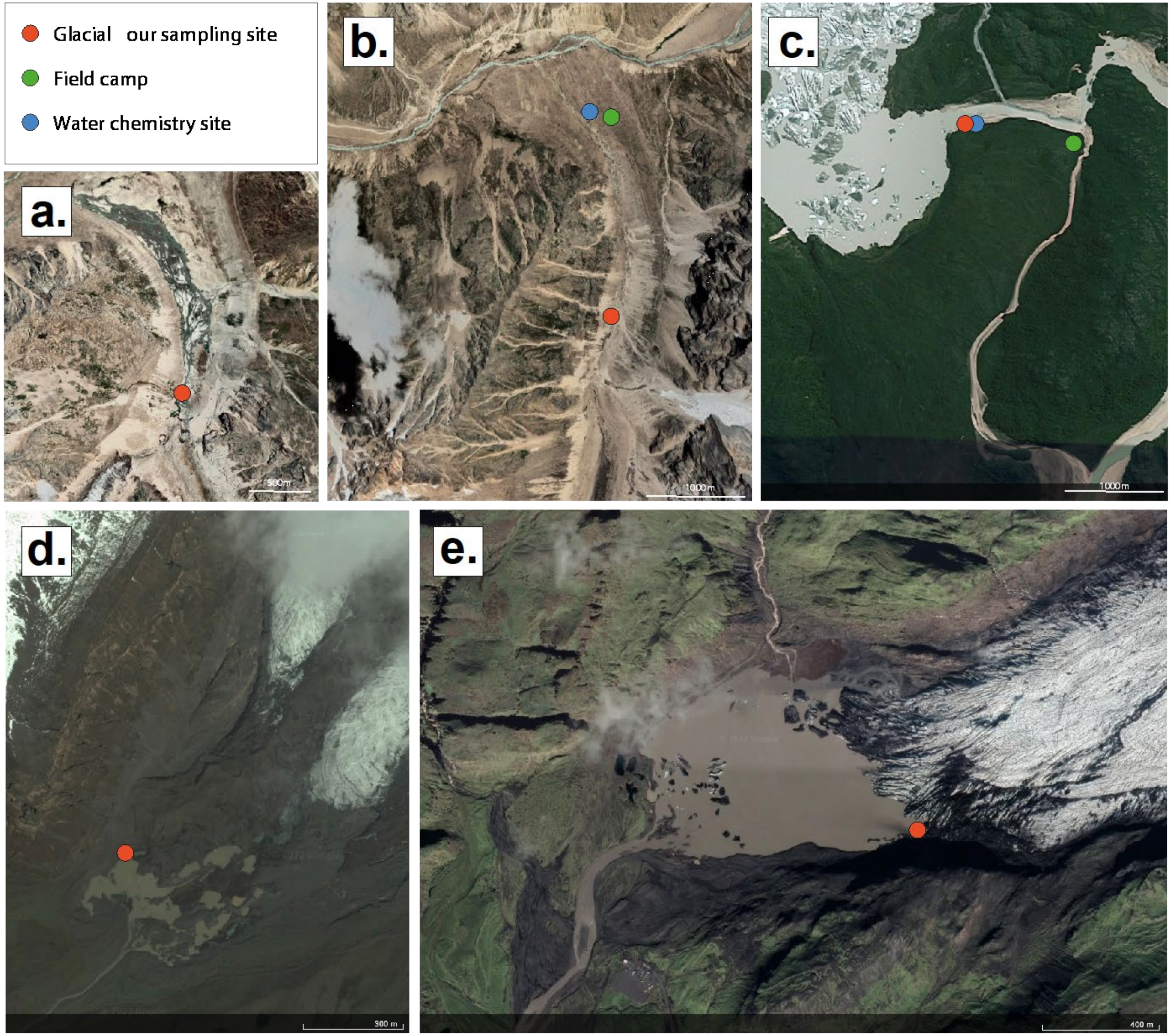


Figure 2.6 – Glaciers visited for the purpose of this thesis and downstream glacial flour sampling site locations, field camps and water chemistry sites where training occurred. a. Bara Shigri, India Himalayas. b. Chhota Shigri, India Himalayas. c. Steffen glacier, Patagonia, Chile. d. Falljökull, SE Iceland. e. Sólheimajökull, SW Iceland.

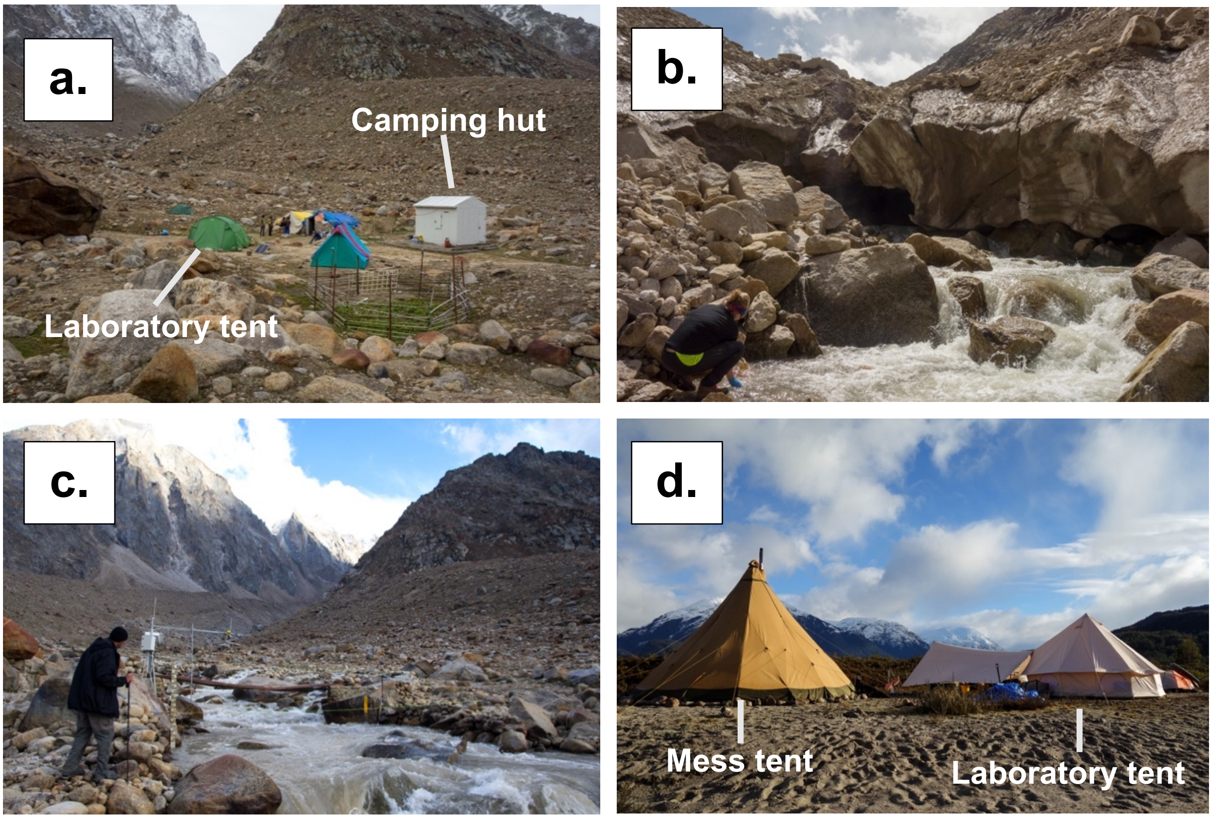


Figure 2.7 – A) Fieldwork sites a) Chhota Shigri basecamp, green tent (left) and grey hut (right) were used as laboratory spaces in 2017 and 2018. B) Sampling portal meltwater at Chhota Shigri, C) Sensor and discharge station at Chhota Shigri built by Ramanathan research group, JNU Delhi, where Bristol CTD was also installed D) Steffen glacier, Patagonia camp, white tent (right) employed as clean lab tent

2.3 Crop yield investigation

2.3.1 Crop yield introduction

Crop growth investigations using glacial flour were conducted within 6 months of returning from fieldwork. Glacial flour samples were kept in dark refrigerated storage (5 ºC) prior to use in the crop growth study. This is a regularly used technique to store samples and unlikely to have resulted in any significant alteration prior to use and analysis (Rowell 1994). Following collection of glacial flour from Sólheimajökull glacier (Iceland) and Chhota Shigri glacier (Indian Himalayas) a crop yield investigation was performed utilising the glasshouse set up in the Grodome agricultural research facility, Life Sciences, University of Bristol. An initial pilot study (February 2016) was undertaken before the full soybean crop growth experiment (November 2017 – March 2018).

2.3.2 Pilot study – USU-Apogee wheat

Prior to undertaking the full replicate crop growth experiments, the experimental set up for crop growth had to be refined. Firstly, a crop trial was performed using USU-Apogee wheat (*Triticum aestivum. L.*) to determine whether crops could be grown using a low nutrient soil matrix (sand : compost, 9:1) with prospective soil treatments. Three glacial flours were tested at a rate of 2 T ha^{-1}: Arolla, Sólheimajökull and Falljökull. Due to wheat requiring high N-input, a chemical NPK fertiliser treatment and a flour + N fertiliser treatment was also performed to assess the experimental set up. Chemical N fertiliser addition was achieved through the application of Ammonium nitrate, NH_4NO_3, chemical P through P_2O_5 and chemical K through K_2O. Each soil treatment was homogenised by mixing in a sterile Whirl-pak® before being put in an individual 9 cm pot to equilibrate for a week. Leaving the experimental soils for this period is common practice in agricultural experiments testing soil treatments because it avoids large temperature changes and fertiliser "burning" of seedlings. All wheat seedlings were germinated in vermiculite bags at 25 ºC, 100 % humidity and when seedlings had visibly chitted, the wheat seedlings were transplanted into their corresponding soil treatments.

Each experimental pot was placed on an individual tray to avoid nutrient loss (Mohammed et al. 2014) following watering. All pots were watered daily with RO water to maintain optimal moisture and avoid any water stress, water was applied to the tray, every week 100 mL of RO water was applied to the top of the pot. This pilot study was only performed as one experiment with three replicate pots per treatment. Plant height was measured to determine differences in wheat growth over the 60-day experiment, results shown in Figure 2.8.

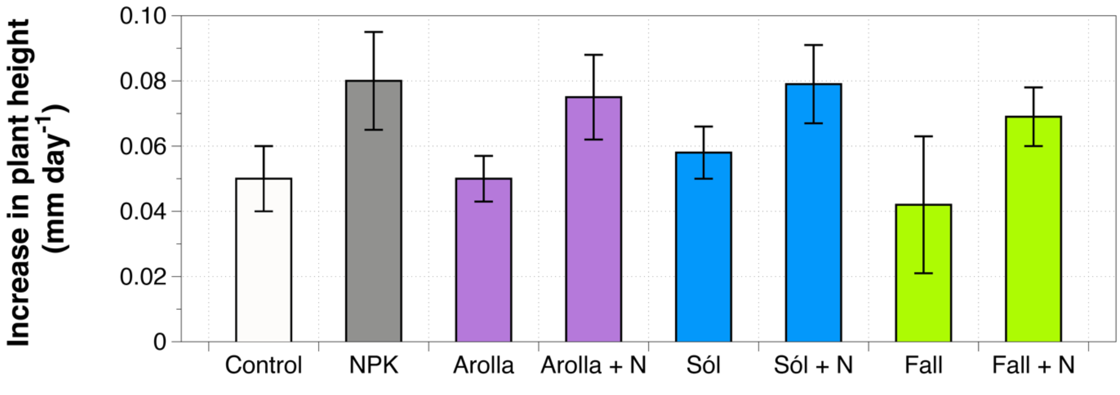


Figure 2.8: Apogee crop growth pilot study. Showing no treatment control and NPK treatments. Then glacial flour additions Arolla, Arolla + N, Sól = Sólheimajökull, Sólheimajökull + N, Fall = Falljökull, Fall + N. Error bars represent min and max values of 3 replicate treatments.

The results from our pilot study with USU-Apogee wheat indicated that glacial flour does have potential to act as a source of nutrients for crops. However, the USU-Apogee wheat is a genetically modified (GM) crop, known to have very high N-demands, crop growth was not significantly successful above the control (no treatment) without N addition. Therefore, subsequent crop growth experiments would be performed using a leguminous crop that forms a symbiotic relationship with N-fixing bacteria would avoid the need for additional N treatments and be applicable to agroecological farming, whereby cover crops and legumes are grown to improve soil-N (Wood and Myers 1987; Ledgard and Steele 1992). Our pilot study also indicated that a sand:compost ratio of 9:1 resulted in very waterlogged pot conditions Perlite is a lightweight inert soil component used within the horticultural industry to break up soils and improve aeration (Kim and Kim 2011). A perlite:compost artificial soil matrix was used for our legume crop growth investigation to promote aeration for the legume roots (Liu and Lal 2014).

2.3.3 Soybean crop yield experiment

Soybean (*Glycine max*) ‘Black jet’ seeds were stratified for 3 days at 4 ºC, then sown into vermiculite bags and propagated at 25 ºC and 100 % humidity until chitting was visible (5 - 8 days). At this stage each germinated seed was rolled in a microbial inoculum (*Bradyhizobium japonicum*) carried by peat, to achieve root nodule formation and to simulate a natural soil microbial system (source: LegumeFix, UK). The germinated beans were then planted into their treatments and artificial soils (Table 2 and 3). Artificial soil was prepared using a volume to volume ratio of 9:1 perlite : commercial seedling compost (Silver Sand, Melcourt and Levingtons Seedling Compost) (Mohammed et al. 2014). Expanded perlite (Silvaperl P35 Grade, Hoben International, Westland Horticulture, UK) is an inorganic, relatively chemically inert, ultra-lightweight amorphous volcanic glass, with high water holding capacity and sufficient pore space enabling soybean root growth (ten Berge et al. 2012). Pots were 9 cm high, with 64 cm^2 surface area, each containing approximately 75 g of artificial soil. All materials were chosen for their low nutrient contents comparable with most other plant growth matrixes, thus minimising external variables.

Prior to planting, artificial soils were mixed and specific treatment components were applied as per each investigation. Briefly, these comprised of a no treatment control, chemical fertiliser treatments (N, P, K, PK and NPK), as well as two glacial flour treatments applied at

0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 T ha^{-1} calculated by applying the equivalent mass of flour (g) for the pot area. Treatment pots were then left to equilibrate for 7 days in a growth chamber before seedlings were transplanted. Fertilisers were applied at FAO crop specific recommended rates (Table 2.4). Chemical N fertiliser addition was achieved through the application of Ammonium nitrate, NH_4NO_3, chemical P through P_2O_5 and chemical K through K_2O, all reagents were analytical grade with <0.5ppm heavy metals. These fertilisers are used in real world application and are an acceptable substitute for the crop investigation. All treatments were performed in triplicate for replicates.

Soybean plants were grown in the controlled environment GroDome chambers (Unigro) with a 12:12 hour light : dark photoperiod at 50 % humidity, 20 ºC, and light by sunlight supplemented by 80 W m^{-2} overhead lighting supplied by < 206 W Attis7 LED grow lamps. All soybean experiments occurred in winter (Nov – March 2018), ensuring consistent light levels. Plants were watered by hand with RO (reverse osmosis filtered) water to maintain optimal moisture conditions but to minimise any nutrient contamination. To reduce nutrient leaching, pots were placed in individual trays which were topped up with water. 100 mL of RO water was added to the top of the pot around the plant once every 7 days as per Mohammed et al. (2014). The crop yield experiment was repeated four times. For the duration of the experiment, plant fluorescence measurements were taken to assess plant stress. At the end of the experiment post-harvest, all plants were recovered from the soils and root nodules were counted as an indicator of microbial soil health and nutrient availability (Mohammed et al. 2014).

2.3.4 Leaf fluorescence imaging

Photosynthesis, whereby photoautotrophs such as cyanobacteria, algae and plants harness light energy for food synthesis using CO_2 as the principal source of carbon, Equation 2.1, can be quantified and recorded parameters can be used as a key indicator of plant health.

$$\mathrm{CO_2 + H_2O \rightarrow [CH_2O] + O_2} \qquad \text{(Equation 2.1)}$$

Light energy is absorbed by chlorophyll pigments, located in chloroplasts that are found in all plant cells, but most typically in the mesophyll, the tissue in the leaf interior. Chloroplast

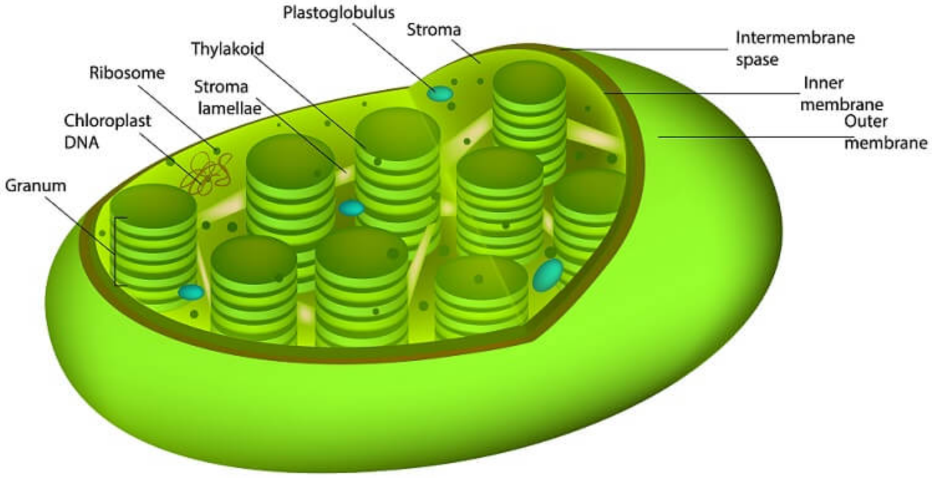


Figure 2.9 –A chloroplast organelle. Located in all plant cells. Photo taken from Biological Dictionary, https://www.biologydictionary.net/plant-cell/ [Accessed 30th September 2021]

organelles have a double membrane, enclosing dense fluid, the stroma, Figure 2.9. The thylakoids segregate the low H^+ concentration stroma fluid from the thylakoid space, a high H^+ concentration matrix, the site of the light-dependent reactions of photosynthesis.

Chloroplast thylakoid membranes contain photosystem protein complexes (PSI or PSII). These consist of a reaction-centre complex surrounded by a light harvesting complex, Figure 2.10. The light harvesting complex contains pigment molecules, chlorophyll *a* (blue green), chlorophyll *b* (olive green) and carotenoids (yellow / orange) (Eberhard, Finazzi, and Wollman 2008). PSI and PSII have a similar structure but differ in their optimum wavelengths because of pigmentation, PSII is best at 680nm, PSI at 700nm (Allen and Forsberg 2001). When a light photon is absorbed by a pigment, it raises the energy of the pigment electrons from ground to an excited state. This energy is then transferred from pigment to pigment until it is delivered to a pair of chlorophyll *a* molecules in the reaction centre complex, known as P_{680} in PSII and P_{700} in PSI. Chlorophyll-*a* molecules undergo oxidation upon excitation, releasing an electron, then passed to the primary electron acceptor and thus starts the cascade of reactions resulting in carbohydrate synthesis, Figure 2.11.

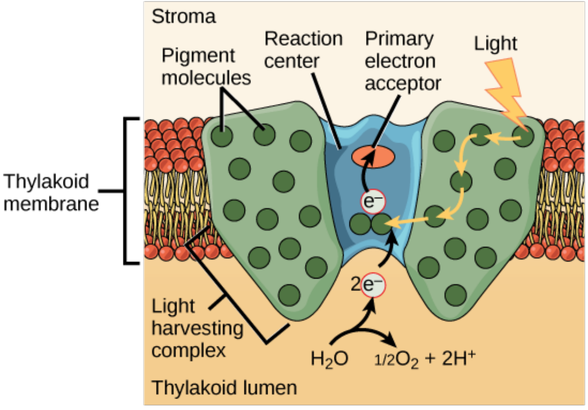


Figure 2.10 – PSII complex. Located in thylakoid membranes. Photo taken from Biological Dictionary, https://www.biologydictionary.net/plant-cell/ [Accessed 30th September 2021]

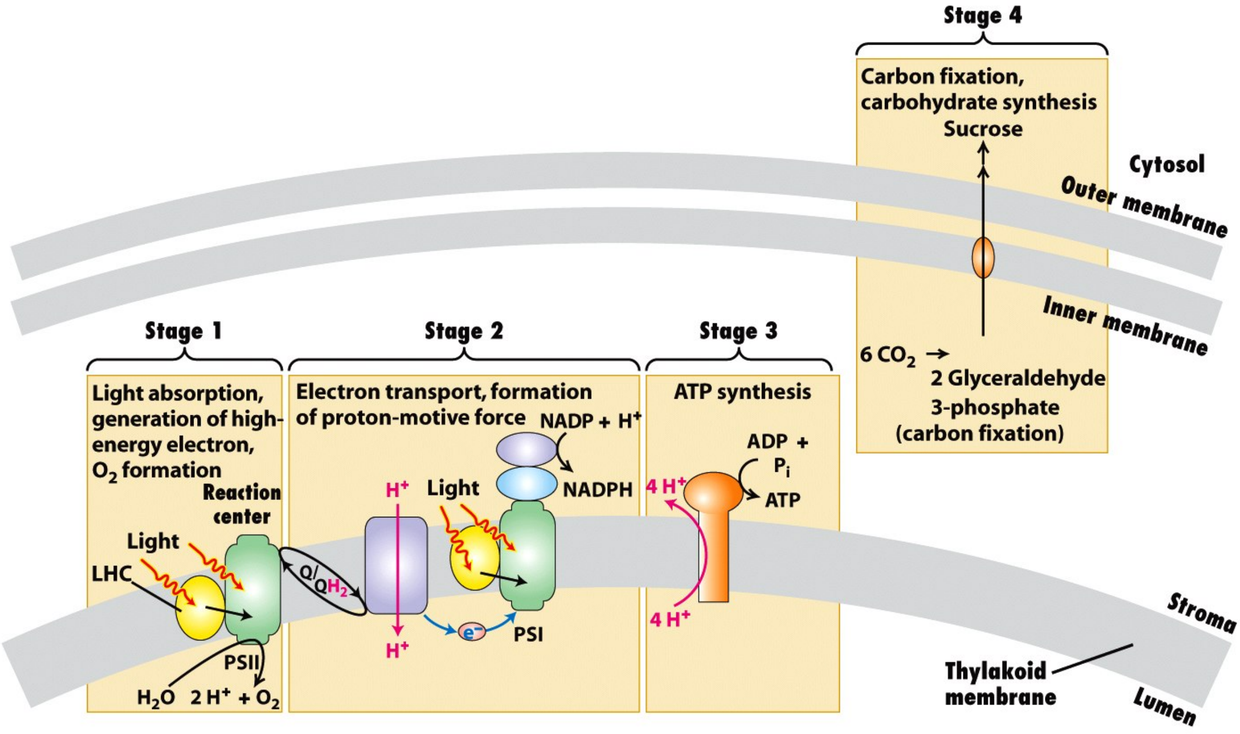


Figure 12-30
Molecular Cell Biology, Sixth Edition
© 2008 W. H. Freeman and Company

Figure 2.11 – An overview of the 4 stages of photosynthesis. **Stage 1:** light is absorbed by the light harvesting complexes (LHC) to the reaction centre of PSII where water is oxidised generated electrons. **Stage 2:** these electrons move down an electron transport chain, which uses lipid-soluble (Q/QH$_2$) or water-soluble (plastocyanin, PC) carriers as shuttles. As they move down the chain they generate a proton-motive force, with additional light from the LHC of PSI, synthesis the electron carrier, NADPH. **Stage 3**: movement of proteins results in the synthesis of ATP. **Stage 4:** In the chloroplast stroma, energy stored from NADPH and ATP fixes CO$_2$ to organic molecules. *[Source: Molecular Cell Biology, Sixth Edition, 2008, page 513]*

Chlorophyll molecules can either drive photosynthesis, be re-emitted as heat, or, be re-emitted as fluorescence (Murchie and Lawson 2013). These processes are linked within competition of each other; therefore, the yield of chlorophyll fluorescence emission subsequently informs values regarding the quantum efficiency of photochemistry and heat dissipation. At room temperature, it is assumed fluorescence signal arises from PSII only (Butler 1978). Fluorescence parameters provide informative structural and function measurements of PSII processes (Murchie and Lawson 2013, Strasser, Tsimilli-Michael, and Srivastava 2004).

Chlorophyll fluorescence imaging during the plant growth experiment was used to evaluate plant photosynthetic activity. The first fully expanded leaf from the top of the plant was analysed for chlorophyll fluorescence at 2, 7, 12, 17, 22 and 27 days from the start of the experiment. Measurements were made at a leaf temperature of 20 ºC. Prior to analysis, plants were dark-adapted in a sealed pitch-black chamber for 30 minutes. Chlorophyll fluorescence was measured using a portable pulse modulated fluorimeter (IMAGING-PAM M-Series Mini Walz). Fv/Fm scores are the most common method for measuring many types of plant stress, and help determine whether plant stress is affecting photosystem II, the first protein complex in the light dependent reactions of photosynthesis (Maxwell and Johnson 2000). The Fv/Fm test compares the minimum fluorescence (Fo) to maximum fluorescence (Fm) (the sequence of fluorescence measurements is shown in Figure 2.12). The fewer reaction centres available, the greater the plant stress. The difference between Fo and Fm is Fv, variable fluorescence. Fv/Fm is a normalised ratio comparable across plants, representing the maximum potential quantum efficiency of photosystem II if all capable reaction centres were open. Each replicate plant was measured through 4 separate regions of interest on the leaf that was selected for measurement.

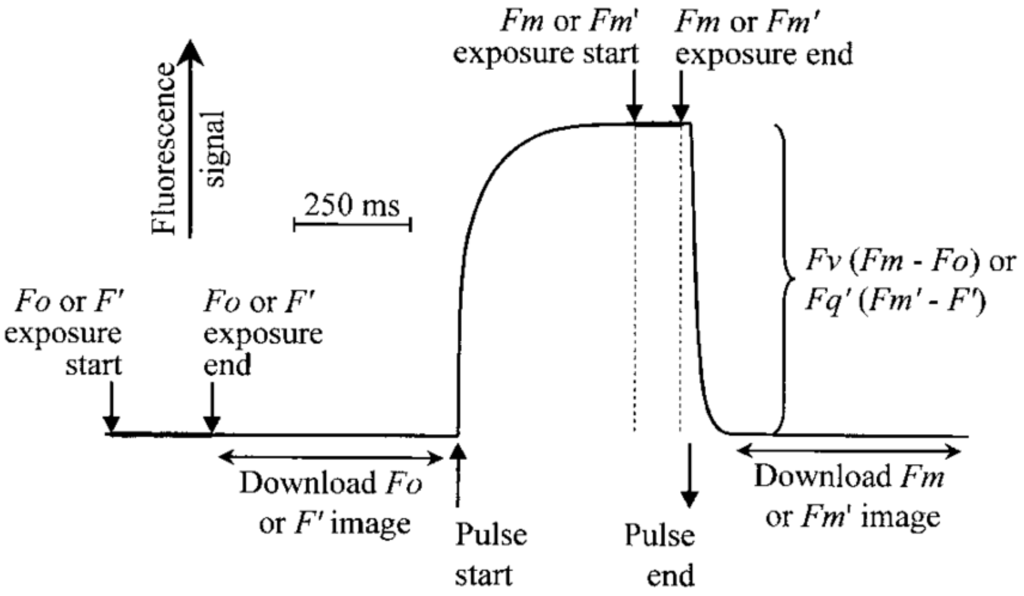


Figure 2.12: Fluorescence imaging trace showing the terminology and sequence of events leading to the generation of Fv/Fm values. Exposure time varies for plant type but is generally from 20 – 120 ms.(Baker et al. 2001)

2.3.5 Agricultural calculations

An important factor in agriculture is the measure of crop yield. At the end of each replicate experiment (50 days), soybean plants were harvested, dried for 7 days at 65 ºC and separated to record biomass. Crop yield (g m^2) was calculated using the agricultural standard yield estimation for soybean crops, Equation 2.2. The yields were calculated for each separate experiment run consisting of multiple replicates.

$$\frac{[\text{Pods m}^{-2}] \times [\text{no.of seeds per pod}]}{[100 \times \text{seed weight } (g)]} \qquad \text{(Equation 2.2)}$$

Although the 9 cm pot size has a small surface area (114 cm^2), up-scaling the yield values to infer potential increases in crop yields in the pot is deemed reasonable and has been performed within other pot investigations (Verlinden et al. 2009; Baronti et al. 2010).

Another key measure for farmers is calculating the yield efficiency following soil treatments, allowing economic costing to be evaluated (Dobermann 2007). Agronomic efficiency (AE) calculations (Equation 2.3) using crop yield were used to assess efficacy of treatments. Here, Y = yield of harvester portion of crop with nutrient applied, Y_0 = yield with no nutrient applied, F = amount of nutrient applied (Devasenapathy 2008; Dobermann 2007).

$$AE = (Y-Y_0) / F \qquad \text{(Equation 2.3)}$$

2.4 Sample analysis

2.4.1 Analytical introduction

Analysis of the glacial flours and plant material was conducted within 6 months of returning from fieldwork or at the end of the crop yield investigation, apart from trace element extractions which due to the COVID pandemic were delayed in some cases by up to 12 months. Glacial flour samples were kept in dark refrigerated storage (5 ºC), which is a regularly used technique to store samples and unlikely to have resulted in any alteration prior to use and analysis (Rowell 1994).). Soybeans were stored dried in the dark at room temperature, a typical method of plant material preservation, however it can be noted that up to 2 % of trace elements can be lost during the oven drying process (Gissel-Nielsen 1970).

Due to the trace concentrations of nutrients and elements found in sediments and plant material, it was crucial that clean lab practice was followed. For nutrient analysis, equipment was washed with an initial 2 % DECON® solution to remove any oils or residues from manufacturing, before a further cleaning step of 10 % HCl for 48 hours, followed by a six times Milli-Q water (Millipore®) (Milli-Q) wash and drying in the laminar flow (Hawkings et al. 2015a; Hawkings et al. 2016). Equipment used in trace element analysis was washed using the standard protocol and rinsed using Milli-Q, before being immersed in a 10 % HNO_3 bath for 24 hours to oxidise any trace elements and then finally a six times ultrapure 18.2 MΩ.cm Milli-Q water (Millipore®) rinse and drying in the laminar flow (Hawkings et al. 2014). Throughout analysis, nitrile gloves were worn and for trace element work clean room gloves were worn.

2.4.2 Glacial flour characterisation

2.4.2.1 Particle size

Due to the different glacial flours having varied mineralogy, it was essential that particle size was determined to allow for a comparison of dissolution potential within soils. Particle size was determined using a Malvern Mastersizer 3000 analyser which uses laser diffraction to measure the particle size and particle size distribution of the glacial flours (Sperazza, Moore, and Hendrix 2004). The Mastersizer uses ultrasound to ensure sediment is broken down into its constituent particles. Particle size fractions were then calculated using five replicate samples.

2.4.2.2 Exchangeable Nitrogen

To determine the nutrient content of glacial flours and the artificial soil components, sediment extractions were used. These extractions allow for a chosen nutrient to be removed from the sediment via a chemical reaction with a reagent. Soil inorganic nitrogen, commonly termed 'exchangeable nitrogen (Ex-N)', (sum of inorganic nitrate (NO_3) and ammonia (NH_4)) was determined in the glacial flours and artificial soil components using the most commonly used extraction solution, a potassium chloride (KCl) extraction (1:10 *w/v* soil : extractant) (Maynard, Kalra, and Crumbaugh 1993; Telling et al. 2011). Briefly, approximately 1g of sediment was added to 10mL of 2M KCl in an acid washed polypropylene test tube. Three procedural blanks were also performed to determine any methodological contamination. The samples were then shaken for 30 min at 180 rpm before being centrifuged for 5 min at 4500 rpm. The supernatant extract was filtered using a 0.45 µm Whatman® Puradisc 30 AQUA (polypropylene (PP)) syringe filter into acid-washed polypropylene centrifuge tubes. A syringe filter was used because it ensured the newly dissolved nutrients would pass through the filter. Following removal of the first extract solution, 10 mL of Milli-Q was added to the sediment sample, the samples were then shaken for another 30 min at 180 rpm, before being centrifuged for a further 5 min. The Milli-Q wash was then added to the first extract solution, diluting the extract matrix 1:2. Prior to analysis, the combined KCl + Milli-Q wash extracts were diluted at a 1:5 ratio to bring them within the instrumental detection range. Samples were analysed using the manual colorimetric method outlined below (section 2.4.2.4) within 5 hours of extraction. Procedural blanks were below method detection limits.

2.4.2.3 Phosphorous

Past research has found that glacial flour can be rich in bioavailable phosphorous (Hawkings et al. 2016). A sequential phosphorous extraction was used to determine phosphorous speciation that has previously been used on proglacial suspended sediments and cryoconite sediments (Hawkings et al. 2016; Stibal et al. 2008; Hodson, Mumford, and Lister 2004). The sequential extraction method targets decreasingly reactive phosphorous fractions with greater intensity of reagents. First, ~ 50 mg of glacial flour was precisely weighed into a 2 mL polypropylene microcentrifuge tube. The first extraction, Extraction 1, was 1.5 mL of 1M $MgCl_2$ solution. Extraction 1 targets the loosely bound P that is the most labile. The samples were then set on a reciprocating shaker at 180 rpm for 16 hours and were then centrifuged at 2,600 rpm for 12 minutes. Following this, the supernatant was carefully extracted using a Gilson® pipette and inserted into an open 2 mL syringe. When the syringe was full, the supernatant was filtered using a 0.45 µm Whatman® Puradisc 30 AQUA (PP) syringe filter into a new 2 mL microcentrifuge tube. The sediment was then washed with 1.5 mL of Milli-Q for 2 hours on the reciprocating shaker at 180 rpm, and the supernatant was extracted as above. The next extraction, Extraction 2, was 1.5 mL of 0.1 M NaOH which targets readily available phosphorous, predominantly Fe– and Al–bound P that is believed to be potentially biolabile. Extraction 2 involved the same procedure as Extraction 1 (16 hours on shaker, filtered and washed). The sum of both Extraction 1 and Extraction 2 are normally described as the ‘labile’ or ‘exchangeable-P’ fraction in sediments that is most immediately available to algae and plants (DePinto, Young, and Martin 1981; Dorich, Nelson, and Sommers 1980; Sharpley and Smith 1993; Hawkings et al. 2016; Hodson, Mumford, and Lister 2004). After this, Extraction 3 was performed using a 1 M HCl extraction for Ca and Mg-bound P, predominantly apatite and other P mineral phases, using the same procedure for Extraction 1 and 2. Finally, Extraction 4 was performed for the residual P fraction on the remaining sediment. Extraction 4 was the most aggressive extraction. Retained sediment from previous extractions was transferred to an acid washed Pyrex® digestion tube with Teflon® lined PP stopper, to which 5 mL of a $H_2SO_4/K_2S_2O_8$ solution was added. Samples were autoclaved for 60 minutes (121 °C, 15 psi) (Jeffries, Dieken, and Jones 1979). After being autoclaved, samples were left to cool before the supernatant was removed and filtered as above, again using a 0.45 µm Whatman® Puradisc 30

AQUA (PP). As per the Nitrogen extraction (section 2.3.3.1), three procedural blanks were also run that were below the method detection limit.

2.4.2.4 Colorimetric analysis of Exchangeable Nitrogen and Phosphorous

Nitrogen and phosphorous analysis were determined using colorimetric methods. Colorimetric analysis is a method of ascertaining the concentration of a chemical element or analyte within a solution, whereby there is a chemical reaction between a reagent and chosen nutrient, which produces a coloured dye. The intensity of the coloured dye is proportional to the concentration of the analyte as per the Beer-Lambert Law (Equation 2.4). These colorimetric methods are regularly used for analysis of freshwater, seawaters and sediment extractions.

$$\boldsymbol{A = \log \frac{I_0}{I} = \varepsilon\, c\, l} \qquad \text{(Equation 2.4)}$$

A = absorbance
I_0 = initial light intensity
I = light intensity of the sample solution
$\boldsymbol{\varepsilon}$ = molar absorption
c = concentration of solution (mol L-1)
l = length of cell

A minimum of five standards were run prior to samples, spanning the sample range. All standards and blanks were matrix matched to the sediment extraction solution. During all colorimetric analysis, a drift standard (bottom of the standard range) was also run alongside a matrix matched lab blank every 10 – 15 samples to avoid contamination and ensure method / instrument drift was managed. The standards were gravimetrically diluted using a 1000 mg L^{-1} certified reference standard (Sigma TraceCERT®) and all runs included an independent check standard manually made using salt solutions as per the instrument methods. The inclusion of an independent check standard reduced potential errors with gravimetric standard dilutions. Concentrations are expressed in terms of the element rather than the compound (e.g., NH_4-N rather than NH_4).

2.4.2.4.1 Exchangeable-N

Colorimetric analysis of exchangeable-N extracts was performed using a flow injection analyser (FIA) (LaChat QuikChem 8500 Series 2 FIA system, Loveland, CO, US). The concentration of dissolved inorganic N within the KCl extract (section 2.3.3.1) was determined as the sum of inorganic N species ($NH_4 + NO_3$). This method involved running two well-known protocols on the FIA. First, the concentration of NH_4^+-N (QuikChem® method 31-107-06-1-I) in the KCl extracts was determined. This method employs the Berthelot reaction, in brief, NH_4 reacts in an alkaline solution with hypochlorite to form monochloramine, which in the presence of phenol and nitroprusside at high pH, gives indophenol blue. The indophenol blue measured at a wavelength of 630 nm is proportional to the NH_4 concentration (NH_4-N mg L^{-1}). This method is applicable to non-standard matrixes, such as KCl extracts which were diluted 1:10 with Milli-Q to avoid any in-line precipitation issues. Seven matrix matched standards were used ranging from 5 to 500 µg L^{-1}, alongside an independent check standard made using NH_4Cl, diluted gravimetrically from 200 mg L^{-1} NH_4-N.

Second, the concentration of NO_3-N in the KCl extracts was determined using the cadmium reduction method for colorimetric analysis (QuikChem® method 31-107-05-1-K). This protocol reduces NO_3 to NO_2 through a copperised cadmium column. This method involves a reaction with NO_2, however inorganic NO_2 is not expected to be high within sediment deposits (Philips, Laanbroek, and Verstraete 2002). Within the FIA method, NO_2 (reduced NO_3 + original NO_2) is then determined through diazotization (conversion of primary aromatic amines into diazonium salt), with sulfanilamide following by coupling with N-(1-naphthyl)-ethylenediaminedihydrochloride, giving rise to a magenta-coloured dye. The magenta dye is read at a wavelength of 520 nm which is proportional to the NO_3 concentration (NO_3-N mg L^{-1}). As per the NH_4 method, the NO_3 method is also applicable to non-standard matrixes, such as KCl extracts which were again diluted 1:10 with Milli-Q to avoid any in-line precipitation issues. Seven matrix matched standards were used, these ranged from 5 to 500 µg L^{-1}. This was also checked with independent standard checks of a KNO_3 solution standard, gravimetrically diluted from 200 mg L^{-1} NO_3-N. The sum of both concentrations in the KCl extract (NH_4-N + NO_3-N) is known as the Exchangeable-N concentration (Turpin-Jelfs et al. 2019).

2.4.2.4.2 Phosphorous

Phosphorous was also run colorimetrically on the LaChat QuikChem® 8500 series 2 FIA (QuikChem® method 31-115-01-1-I). The concentration of orthophosphate (PO_4^{3-}) was determined in each sequential phosphorous extraction solution (section 2.3.3.2) using well-established methods for measuring orthophosphate in aqueous samples (Murphy and Riley 1962). The protocol has been used for analysing sequential phosphorous extracts with alternative sample matrixes on glacial suspended sediments therefore was suitable for this body of work (Hawkings et al. 2016). The colorimetric method used is based on the reaction between the orthophosphate ion with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a measurable complex. This complex is further reduced with ascorbic acid to form a blue complex, which absorption is measured at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample. All extractions were diluted with Milli-Q water before analysis to bring them within the instrumental detection range, $MgCl_2$-P was diluted 1:3, NaOH-P; 1:10, HCl-P; 1:100, Residual-P 1:15. Seven matrix matched standards were used, that spanned range in analysis (Table 2.4) for each extraction solution, these were also verified with an independent check standard of potassium phosphate (KH_2PO_4) solution gravimetrically diluted from 200 mg L^{-1} PO_4-P to mid-range for each extraction (Table 2.4).

2.4.2.4.3 Data Quality

Analytical procedures were employed to increase the reliability and validity of this dataset. The limit of detection, precision, accuracy and were calculated for the nitrogen and phosphorous extraction methods (Table 2.4) and are shown in equations 2.5 – 2.7. As outlined above, matrix matched lab blanks were run to evaluate method detection limits and instrumental bias. Method blanks were performed to correct for any procedural errors, such as reagent contamination.

Determination of instrument limit of detection (MB = Milli-Q or Matrix matched blank, $\boldsymbol{\sigma} = \textbf{standard deviation},\ \bar{\boldsymbol{x}} = \textbf{sample mean}, \boldsymbol{n} = \textbf{number of replicate blanks}$*)*

$$\text{Limit of detection} = (\boldsymbol{n} \times \boldsymbol{\sigma}\text{MB}) + \bar{\boldsymbol{x}}\text{MB} \qquad \text{(Equation 2.5)}$$

Determination of precision

$$\textbf{Precision}\ (\%) = \frac{\boldsymbol{\sigma}}{\bar{\boldsymbol{x}}} \times \mathbf{100} \qquad \text{(Equation 2.6)}$$

Determination of accuracy (C_m = Concentration measured, C_a = Concentration actual)

$$\textbf{Accuracy}\ (\%) = \frac{\boldsymbol{C_m} - \boldsymbol{C_a}}{\boldsymbol{C_a}} \times \mathbf{100} \qquad \text{(Equation 2.7)}$$

Table 2.4: Nitrogen and Phosphorous data quality for extraction analysis

	Exchangeable-N		Sequential-P			
	NH_4-N	NO_3-N	Ext-1 (MgCl-P)	Ext-2 (Na-OH-P)	Ext-3 (HCl-P)	Ext-4 (Residual-P)
Calibration range (µg L^{-1})	1.12 – 503	1.08 – 505	1.02 - 251	1.06 - 258	5.15 - 512	1.18 - 267
LoD (µg L^{-1})	0.12	0.09	0.99	1.25	2.17	0.56
Precision (%) *	±3.18	±1.79	±2.93	±2.14	±3.06	±0.76
Accuracy (%) †	0.87	1.12	2.36	0.91	2.49	-2.04
Mean Check standard (µg L^{-1}) (n = 6)	103.7	102.8	102.2	52.2	104.0	105.8
Method blank (µg L^{-1}) (n = 4)	3.78 ± 1.12	5.31 ± 0.85	4.47 ± 0.98	1.25 ± 0.33	5.43 ± 0.84	9.6 ± 1.1

*Precision based on a minimum of 5 replicate analysis of a mid-range standard

†Accuracy was calculated using the replicate of the matrix matched blank

2.4.2.5 Labile Potassium and Iron

Labile potassium (K) and iron (Fe) was determined using a sequential extraction method, adapted from Tessier, Campbell, and Bisson (1979a). As per the sequential phosphorous extraction (section 2.4.2.3), the sequential metals extraction targets increasing unreactive fractions of metals using different reagents. The first extraction, Extraction 1 removes highly labile loosely-sorbed metals and uses a 0.5 M $MgCl_2$ solution. Approximately 1 g of air-dried (clean 100 laminar flow) uncrushed sediment was carefully weighed into a trace metal clean acid washed 15 mL polypropylene (PP) centrifuge tube (Corning™ Falcon). The first extraction solution was added, 8 mL of 0.5 M $MgCl_2$ and centrifuge tubes were placed on a reciprocating shaker for 8 hrs at 200 rpm. Following this, the sample tubes were centrifuged at 2000 rpm for 20 min, and the supernatant carefully extracted into an acid-washed clean 15 mL centrifuge tube using a 5.0 mL syringe (PP/Polyethylene (PE)) and a 0.22 µm Whatman® PP syringe filter (PP membrane) as detailed in section 2.4.2.3. Retained sediment was shaken with 8.0 mL of MilliQ water for 30 mins and centrifuged as above, supernatant extracted and filtered then added to the initial extract. The sediment was then subjected to the second extraction. Extraction 2 removes metals bound to Mg and Ca carbonates (apatite) using a 1 M sodium acetate (NaOAc) solution. The retained sediment is added to 8 mL of 1 M NaOAc and placed on a reciprocating shaker for 10 hrs at 200 rpm, centrifuged, extracted and washed following the same procedure as per extraction 1. The combination of both extraction 1 ($MgCl_2$-Fe, $MgCl_2$-K) and extraction 2 (NaOAc-Fe, NaOAc-K) are commonly termed 'labile' metals due to their availability to algae and plants within solution (Chau and Lum-Shue-Chan 1974). Both extractions were diluted 1:5 with 1 M HNO_3 before analysis to lower extraction solution concentrations. Metals concentrations of the extracts were determined using spectroscopy on an Agilent 710 Inductively coupled plasma optical emission spectrometry (ICP-OES) (section 2.4.3.1). Five procedural blanks were performed to monitor potential method and contamination errors, these were all found to be below detection limits.

2.4.2.5.1 Data quality

As with previous analysis, we ensured our data was reliable and valid through calculating the limit of detection, precision, and accuracy (Table 2.5) as per equations 2.5 – 2.7 We also ran matrix matched lab blanks to evaluate method detection limits and instrument bias. Any method errors were controlled via the inclusion of method blanks.

Table 2.5: Labile Fe and K data quality. Shown to 3 significant figures.

	Labile-Fe		Labile-K	
	Ext-1 (MgCl-Fe)	Ext 2 (NaOAc-Fe)	Ext-1 (MgCl-K)	Ext-2 (NaOAc-K)
Calibration range ($\mu g\ L^{-1}$)	1.35 – 248	1.17 – 256	1.42 - 254	1.07 - 252
LoD ($\mu g\ L^{-1}$)	0.02	0.05	0.85	1.25
Precision (%) *	±0.83	±0.48	±1.27	±3.15
Accuracy (%) †	2.16	1.55	2.76	-2.42
Mean Check standard (n = 6)	104	103	102	52.2
Method blank (n = 5)	3.78 ± 1.12	5.31 ± 0.85	4.47 ± 0.98	1.25 ± 0.33

*Precision based on a minimum of 6 replicate analysis of a low-end standard

†Accuracy was calculated using the replicate of the matrix matched blank

2.4.3 Glacial flour and plant material element content

Analysis of both glacial flour and plant material (soybean crop) for total element (metal and metalloid) content was carried out in the School of Natural and Environmental Sciences, Newcastle University. Glacial flour and plant material (termed 'sample material') were extracted for total element content, also employing techniques analogous to previous extraction protocols for phosphorous and nitrogen (sections 2.4.2.2 and 2.4.2.3). For total element content, approximately 0.1 – 0.5 g of sample material firstly crushed using a sterile pestle and mortar. The crushed sample material was digested using a modified aqua regia solution. Each sample was weighed into a Teflon® extraction vessel to which 2 mL of 30 % H_2O_2, 2.5 mL 37 % HCl and 10 ml of 67 % HNO_3 was added. All reagents used were trace metal analytical grade (Sigma Trace metal grade®). The sample vessels were shaken by hand before being placed into a Mars 6 microwave. For each microwave digestion, the temperature was steadily increased for 20 min up to 210 ºC, where it was held for 15 min at medium pressure (approximately 20 psi). Sample vessels were then left to cool to room temperature. Once each vessel was at the appropriate temperature, the samples were filtered using Nalgene® filter towers with a Whatman grade 41 filter paper. The filter towers were cleaned in between each use using a Milli-Q rinse, followed by a 0.1M HNO_3 wash and a final Milli-Q rinse six times to avoid cross contamination. All samples were then diluted up to 50 mL using 0.1M HNO_3 prior to analysis. Procedural blanks were run to check method errors. We determined metal concentrations in the extraction solution using an Agilent 7500 ICP-MS.

2.4.3.1 Sample concentration calculation

Following geochemical extractions, the concentration (mg L) of the chosen element (X) in solution was determined by equation 2.8.

$$\frac{(Concentration\ of\ X\ in\ Ext\ Solution\ (mg\ L^{-1}))\times\ (Ext\ volume\ (mL))}{(Mass\ Sediment\ (g))} \qquad \text{(Equation 2.8)}$$

2.4.3.2 Data Quality

To ensure data was as robust as possible, the limit of detection, precision, and accuracy as per equations 11 – 13 were calculated (Table 2.6). To ensure machine drift could be monitored, a 50 ug L^{-1} internal standard was mixed into the sample using a T-junction inline mixing kit. Polyatomic interferences were removed using a collision-reaction cell with He gas.

Four method blanks and a minimum of six matrix matched lab blanks were performed to determine method detection limits and instrument bias. Matrix matched lab blanks were below the method detection limit.

Table 2.5: Data quality for trace element extraction of glacial flour and plant material

	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Ni	P	Pb	Se	S	Sr	Zn
Detection limit high *(mg g^{-1})*	0.0032	2.23	0.0019	0.0021	0.0055	0.45	0.20	0.32	0.229	1.27	0.078	0.013	1.04	0.0056	0.0028	3.53	0.029	0.20
Detection limit low *(mg g^{-1})*	0.0008	0.56	0.0005	0.0005	0.0014	0.11	0.05	0.08	0.057	0.32	0.019	0.0031	0.26	0.0014	0.0007	0.88	0.0073	0.05
Precision *(%) **	±2.25	±5.93	±0.89	±1.59	±1.67	±1.14	±0.83	±2.94	±2.58	±2.21	±2.93	±1.38	±2.61	±1.09	±1.92	±9.11	±1.65	±1.96
Accuracy *(%) †*	6.72	0.43	0.18	2.29	2.29	2.20	1.11	2.46	3.83	0.72	4.77	0.81	0.24	0.99	11.10	4.13	0.15	6.61
Method blank *(mg g^{-1})*	0.0016	1.11	0.009	0.001	0.0028	0.22	0.10	0.16	0.114	0.63	0.039	0.0063	0.52	0.0028	0.0014	1.75	0.015	0.10

*Precision based on a minimum of 6 replicate analysis of a low-end standard

†Accuracy was calculated using the replicate of the matrix matched blank

Chapter 3.

Glaciers as a source of lithogenic macronutrients and trace elements

***Tingey S**, Wadham JL, Telling J, Hawkings JR, Yates C, Flynn S, Ramanathan AL, Sgouridis F.*

3.1 Abstract

Glaciers act as ‘sediment factories’ exporting large quantities of suspended particulate material, termed ‘glacial flour’, in annual meltwaters to downstream environments. Past studies have focused on the dissolved nutrient and trace element (TE) content of glacial meltwater, whilst the particulate component remains poorly constrained. Against this backdrop, glacial flour has potential to be used as a novel source of crushed rock within agriculture, potentially enriching soils with fresh parental mineral material. Here, we present a geochemical dataset of recently deposited glacial flours from 11 trans-global glacial sites. We performed extractions for labile P, labile K and total trace elements (TE) concentrations to infer the potential macronutrient and TE supply from glacial flour. We found that some glacial flours from flood basaltic terrain, such as Iceland, are rich in macronutrients P and K and TE and may have potential to enrich impoverished soils elsewhere in these elements if applied artificially to soils. We also show that other glacial flours, including those derived from sulphide-rich sedimentary bedrocks such as the Andes and Himalaya, contain potentially toxic TE (As, Cd, Cr, Co, Cu, Ni, Pb, Se, Sr, Zn). We infer that glacial flour sourced from basaltic bedrock has the highest potential as a soil fertility treatment and requires further investigation.

3.2 Introduction

Glacierised drainage basins cover 26 % of the global land surface outside of Greenland and Antarctica, and are integral to approximately one-third of the World's population (Anexandratos and Bruinsma 2012). Often regarded as the 'water towers of the world', glacial meltwater acts as an essential water supply to downstream populations, supporting farming, energy production, drinking water and tourism, for example in the Hindu-Kush-Himalaya (Biemans et al. 2019; Bolch et al. 2012). However, in addition to providing a reliable water source, glacial meltwaters have been shown to transport a considerable suspended sediment load, comprising 'glacial flour', in concentrations from 0.1 g L^{-1} in Himalayan glacial rivers and up to 1 g L^{-1} from large ice sheet outlet glaciers in Greenland (Brown, Tranter, and Sharp 1996a; Gurnell and Clark 1987; Hawkings et al. 2015a; Singh, Ramanathan, and Pottakkal 2016a; Cowton et al. 2012). Glaciers act as natural 'sediment factories' effectively grinding the underlying bedrock into fine, reactive particles, 95 % of which are < 66 μm and have been shown to be a source of labile lithogenic macronutrients (P, K) and trace elements (TE), such as Fe, Mn and Zn, which are important for downstream biological productivity (Hawkings et al. 2015a; Hawkings et al. 2016; Hawkings et al. 2017; Hawkings et al. 2014). Prior studies investigating nutrient and TE fluxes from glacial flour have focused on large ice sheets (Antarctic, Greenland), whilst glacial flour supplied from mountainous regions (e.g., Himalayas) remains poorly chemically characterised (Wulf, Bookhagen, and Scherler 2012; Singh et al. 2015; Srivastava et al. 2014). There is an urgent need to understand the biogeochemical attributes of glacial flours, particularly those originating from mountain glaciers that export this material to downstream communities.

Research into developing understanding of glacial flour nutrient and TE content is driven by three key factors. First, global food production will have to increase by up to 50 % to meet projected 2050 demands, whilst becoming more sustainable and resilient to impacts of climate change (Foley, Ramankutty, Brauman, Cassidy, Gerber, Johnston, Mueller, O'Connell, et al. 2011). Recent research has indicated that crushed rock may be a potential soil amelioration strategy that can improve crop yields. However, widespread adoption of the technique has been limited by high economic and carbon costs. 'Naturally' crushed rock, glacial flour, could be an alternative strategy for improving impoverished soil nutrient status

(Schuiling and Krijgsman 2006; Renforth, von Strandmann, and Henderson 2015; Renforth 2012; Moosdorf, Renforth, and Hartmann 2014; Beerling et al. 2020). Second, climate change is projected to have a detrimental impact upon crop yields due to changing precipitation patterns, drought, heat and extreme weather (Cole et al. 2018; IPCC 2018b), rendering some current lands inappropriate for agriculture. Demands upon the agricultural system for food, fibre and biofuels will require agricultural land expansion into regions that were once unsuitable for crop growth, such as deglaciating landscapes at higher latitude (e.g. sub-/Arctic) or higher-altitude areas (e.g. Himalaya) (Zimmer et al. ; Friedrich 2021). Although these landscapes offer potentially fertile soils and may have lengthier growing seasons in a warming climate, the importance of glacial flour nutrient and TE release in these soils is unknown (Arndt et al. 2019; Drever 1994). Third, future climate change is expected to cause shifts in suspended sediment fluxes from glaciers, impacting regions downstream such as agricultural lands irrigated by glacial flour rich meltwaters e.g. the Punjab plains lying on the Indus River downstream of the Himalayas (Meigs et al. 2006; Bolch et al. 2012; Milner et al. 2017; Hawkings et al. 2016; Pritchard 2017). The potential total nutrient and TE supply from glacial flour to agricultural land within glacial catchments is largely unknown.

Glacial flour has been highlighted as a source of nutrients and micronutrients (Fe, P, Si) to microbial ecosystems, benthic stream communities and ocean primary producers (Schroth et al. 2014; Raiswell and Canfield 2012; Lawson et al. 2014). Lithological provenance is likely to determine glacial flour nutrient and TE content alongside mineral dissolution potential. Although glacial cover and subglacial weathering mechanisms have been shown to influence glacial meltwater chemical composition, it is unknown whether this will also have an impact on the total elemental composition and concentration of suspended particulate material (SPM) (Wadham et al. 2010a; Hawkings et al. 2014). Furthermore, recent research has focused on labile nutrients (Fe, P, Si) that are immediately bioavailable following export, however as glacial flour weathers in downstream environments or potentially following application to agricultural soils, it is likely to release a greater proportion of less immediately available elements; for example P from weathering of apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) (Hawkings et al. 2016). The extended release of nutrients from glacial flour to soils may be of significant benefit to farmers, reducing the need for repeat application and potentially enhancing the nutritional value of crop yields for human consumption (Shiferaw, Okello, and Reddy 2009; Altieri and Nicholls 2012; Gomiero, Pimentel, and Paoletti 2011; Food and Agriculture

Organization 2015; DeLonge, Miles, and Carlisle 2016; Mayer, Pfeiffer, and Beyer 2008; Ramakrishnan 2002a).

Conversely, there are also geogenic TE that can have adverse health effects if released within to human food and water systems. Recent research has begun to assess toxic TE fluxes to downstream ecosystems and communities from glaciers, particularly those overlying softer sedimentary bedrocks rich in potentially toxic TE such as, Cd, Co, Cr, Hg, Ni, and Pb (e.g., The Cordillera Blanca, Peruvian Andes) (Hawkings et al. 2021). The potential release of toxic TE has been suggested as a limitation of using crushed rock as a soil amendment strategy, highlighting a need to geochemically assess an array of glacial flours if they are to be used as within strategies to improve crop yields on agricultural land (Beerling et al. 2018b; Manning et al. 2017; Manning and Theodoro 2020).

Here, this thesis presents a comprehensive geochemical analysis of glacial flours sourced from a broad range of different catchment lithologies and glacial environments to infer the potential of glacial flour within agricultural improvement and expansion strategies (Hawkings, Skidmore, Wadham, Priscu, Morton, Hatton, Gardner, Kohler, Stibal, Bagshaw, et al. 2020). We analyse glacial flour total elemental (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, S, Se, Si, Sr and Zn), exchangeable N and sequentially-extracted P concentration data in order to evaluate the potential for glacial flour to act as a beneficial source of nutrients or toxic elements, within agricultural soil improvement or agricultural expansion initiatives.

3.3 Methods

3.3.1 Global glacial sediment sampling

Glacial flours, recently deposited from glacially-fed rivers and now exposed subaerially on river banks, were collected from 11 contrasting glaciers as outlined in Table 3.1, selected to cover a diverse range of geologies: soft sedimentary bedrock (Shallap glacier and Pastoruri glacier Cordillera Blanca, Peru); metamorphic dominant bedrocks (Haut glacier d'Arolla, Swiss Alps, Bara Shigri glacier NW Indian Himalaya); mixed igneous-metamorphic-sedimentary bedrock (Chhota Shigri glacier, NW Indian Himalaya, Tirich Mir, Hindu Kush Himalaya, Pakistan); and hard igneous metamorphic bedrocks of granite and gneiss (Leverett and Kiattut Sermiatt glaciers Greenland, Steffen glacier, Northern Patagonian Ice Field). All glacial flour sampling sites were located within 30 m of the glacial portal, as close to the glacial stream as possible to ensure they were as freshly deposited as possible. All glacial flours were collected during the peak to late melt season to ensure that deposits were fresh and not exposed to further weathering within the proglacial landscape. All sediments were sampled using a plastic trowel that was cleaned with Milli-Q and paper wipes. Sediment samples were then placed into Whirl-Pak® bags where they were transported and stored in a fridge (~ 2 – 4 °C) for a maximum of 6 months prior to trace metal extractions, or freezer (- 20 °C), for P extractions.

3.3.2 Total metals extractions

Equipment was trace metal-cleaned as detailed above, all reagents were of trace metal analysis quality. Total metals (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, S, Se, Si, Sr and Zn) were extracted from glacial flour samples using a modified Aqua Regia microwave digestion (Chen and Ma 2001). Approximately 200 mg of crushed sediment sample was added to 2 mL of 30 % hydrogen peroxide, 2.5 mL 37 % HCl and 10 ml of 67 % HNO_3. Digestions were carried out in pressurized Teflon vessels using a Mars 6 microwave digest. For each digestion the temperature was increased for 20 min to 210 ºC, and the temperature held for 15 min. Samples were filtered with a 0.45 µm Whatman® 41 filter paper and diluted 1:5 with 0.1 M HNO_3 prior to analysis. Three procedural blanks were performed.

Table 3.1: Glacial site, location, geology and major bedrock type

Glacier	Location	Geology	Bedrock type	Reference
Haut Glacier d'Arolla	Swiss Alps	Schistose granite, some gneiss, greenschist, amphibolite and gabbro intrusion	Met-Sed	Tranter et al. (2002)
Bara Shigri	Hindu Kush Himalaya (India)	Schistose granite, fine grained biotite schist, black slates and phyllite	Met-Sed	Singh and Ramanathan (2015)
Chhota Shigri	Hindu Kush Himalaya (India)	Gneiss, some granite, chalcopyrite, some veins of black slates and phyllite	Mixed	Singh et al. (2015)
Falljökull	S Iceland	Basalts, icelandite, breccias, rhyolite	Igneous	MacDonald et al. (2016)
Kiattut Sermiat	SW Greenland	Granite, small complexes of diorite, pyroxene, biotite monozonite and basaltic intrusions	Igneous-Met	Henriksen et al. (2009), Hawkings et al. (2016)
Leverett	SW Greenland	Precambrian crystalline granite / gneiss	Igneous-Met	Henriksen et al. (2009), Hawkings et al. (2016)
Pastoruri	Cordillera Blanca, Andes	Pyrite schists, phyllite and pyrite bearing quartzite, and a central granodiorite tonalite batholith, Sandstones, lutites	Met-Sed	Fortner et al. (2011), Santofimia et al. (2017)
Shallap	Cordillera Blanca, Andes	Pyrite schists, phyllite and pyrite bearing quartzite, and a central granodiorite tonalite batholith, Sandstones, lutites	Met-Sed	Fortner et al. (2011), Schauwecker et al. (2014)
Sólheimajökull	S Iceland	Basalts, breccias, rhyolite, palagonite	Igneous	Wynn et al. (2015)
Steffen	Northern Patagonian Ice cap	Granite, hornblende-biotite, granodiorite, tonalite, leucogranite	Igneous-Met	Pryer et al. (2020), Pankhurst et al. (1999)
Tirich Mir	Hindu Kush Himalaya (Pakistan)	Granite, slate, siltstones, quartzites, ferrogenous limestones and calcareous schists	Mixed	Heft (1986)

3.3.3 Sequential P extraction

Phosphorous (P) was sequentially extracted using a 'micro-extraction' method, which targets decreasingly reactive defined fractions of P (Hawkings et al. 2016; Stibal et al. 2008). After air drying in a laminar flow cabinet, 50 mg of glacial flour (uncrushed) was added to 2 mL digestion tubes. Extraction 1 was 1.5 mL of 1 M $MgCl_2$ solution that removed loosely sorbed P, 'MgCl-P' which was added to the 2 mL PP microcentrifuge with the sample and set on a reciprocating shaker for 180 rpm for 16 hours, before being centrifuged at 2,600 rpm for 12 minutes. The supernatant was carefully extracted and filtered using a 0.45 µm Whatman® Puradisc 30 AQUA (PP) in a new 2 mL PP microcentrifuge tube. The retained sediment was then washed in 1.5 mL of MQ, which was then added to the extraction when removed. The retained sediment samples were then used for Extraction 2, which was 1.5 mL 0.1 M NaOH and used to remove Fe– and Al–bound P that may be potentially biolabile (NaOH-P); the sum of these two fractions is termed 'Labile-P'. Extraction 3 was 1.5 mL 0.1 M HCl (HCl-P) which has been shown to remove Ca- and Mg- bound P, (apatite). After each extraction stage, the retained sediment was washed with MQ and the MQ wash was added to each extraction stage. The final extraction, Extraction 4, on the sediment sample was a 5 mL potassium persulfate / sulfuric acid ($H_2SO_4/K_2S_2O_8$) digest used to determine the 'residual' and organic bound P (Res-P). In extraction 4, the retained sediment was placed in an acid washed Pyrex® digestion tube with Teflon® lined PP stopper, the $H_2SO_4/K_2S_2O_8$ solution was added and samples were autoclaved for 60 minutes (121 °C, 15 psi) (Jeffries, Dieken, and Jones 1979). After being autoclaved, samples were left to cool before the supernatant was removed and filtered as above, again using a 0.45 µm Whatman® Puradisc 30 AQUA (PP). The sum of all fractions is termed Total-P. Three method blanks were performed.

3.3.4 Exchangeable N extraction

Particulate inorganic nitrogen, termed 'exchangeable nitrogen (Ex-N)', (sum of inorganic nitrate (NO_3) and ammonia (NH_4)) was determined in the glacial flours. We used a potassium chloride (KCl) extraction (1:10 *w/v* soil : extractant) (Maynard, Kalra, and Crumbaugh 1993; Telling et al. 2011). Briefly, approximately 1g of sediment was added to 10mL of 2M KCl in an acid washed polypropylene test tube. Three procedural blanks were also performed to determine any methodological contamination. The samples were then shaken for 30 min at 180 rpm before being centrifuged for 5 min at 4500 rpm. The supernatant extract was filtered using a 0.45 µm Whatman® Puradisc 30 AQUA (polypropylene (PP)) syringe filter into acid-washed polypropylene centrifuge tubes. As with previous extractions, a MQ wash was performed, whereby 10 mL of Milli-Q was added to the sediment sample, the samples were then shaken for another 30 min at 180 rpm, before being centrifuged for a further 5 min. The MQ wash was then added to the first extract solution, diluting the extract matrix 1:2. Prior to analysis, the combined KCl + Milli-Q wash extracts were diluted at a 1:5 ratio to bring them within the instrumental detection range. Samples were analysed within 5 hours of extraction. Procedural blanks were below method detection limits.

3.3.5 ICP-MS metals analysis

Element concentrations were determined via spectroscopy on an Agilent 7500 inductive coupled plasma mass spectrometer ICP-MS (School of Natural and Environmental Sciences, Newcastle University). A series of seven multi-element matrix matched standards were used to calibrate the ICP-MS (0 – 500 µg L^{-1}). The ICP-MS was configured with a micromist nebulizer, a cooled double concentric spray chamber and nickel cones. During analysis drift was monitored and corrected for using a 50 ppb standard in solution which was added to each sample using a T-junction inline internal standard kit. Polyatomic interferences were removed using a collision gas reaction cell which was employed with He gas. Precision and accuracy are presented in Table 3.2.

Table 3.2: Data quality for trace element extraction of glacial flour

	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Ni	P	Pb	Se	S	Sr	Zn
Detection limit high *(mg g^{-1})*	0.0032	2.23	0.0019	0.0021	0.0055	0.45	0.20	0.32	0.229	1.27	0.078	0.013	1.04	0.0056	0.0028	3.53	0.029	0.20
Detection limit low *(mg g^{-1})*	0.0008	0.56	0.0005	0.0005	0.0014	0.11	0.05	0.08	0.057	0.32	0.019	0.0031	0.26	0.0014	0.0007	0.88	0.0073	0.05
Precision *(%) **	±2.25	±5.93	±0.89	±1.59	±1.67	±1.14	±0.83	±2.94	±2.58	±2.21	±2.93	±1.38	±2.61	±1.09	±1.92	±9.11	±1.65	±1.96
Accuracy *(%) †*	6.72	0.43	0.18	2.29	2.29	2.20	1.11	2.46	3.83	0.72	4.77	0.81	0.24	0.99	11.10	4.13	0.15	6.61
Method blank *(mg g^{-1})*	0.0016	1.11	0.009	0.001	0.0028	0.22	0.10	0.16	0.114	0.63	0.039	0.0063	0.52	0.0028	0.0014	1.75	0.015	0.10

*Precision based on a minimum of 6 replicate analysis of a low-end standard

†Accuracy was calculated using the replicate of the matrix matched blank

3.3.6 FIA P and N analysis

The concentration of P in each sequential P extract was determined colorimetrically on a LaChat QuikChem® 8500 series 2 flow injection analyser, employing the molybdate blue method for detecting orthophosphate (PO_4^{3-}) (QuikChem method 31-115-01-1-I). Extracts were diluted with MQ prior to analysis to ensure they were within the detection range. Seven matrix matched standards were used that spanned the range in analysis (0 – 250 µg L^{-1} for MgCl-P, NaOH-P and Res-P, 0 – 500 µg L^{-1} for HCl-P). Each extraction was verified with an independent mid-range check standard. Precision was based on a minimum of 5 replicate analysis of a low-end standard and was ±2.9 %, ±2.1 %, ±3.1 % ±0.8 % and accuracy was 2.4 %, 0.9 %, 2.5 %, -2.0 % for Extractions 1, 2, 3, 4. Concentrations were corrected using the method blank (n = 4) to calculate the final concentration in the extract. P was extracted using both sequential extraction and microwave extraction methods, total values are noted as P-NCR (not crushed glacial flour, sequential) and P-CR (crushed glacial flour, microwave extraction).

Exchangeable-N was measured in the KCl extracts as the sum of inorganic N species (NH_4 + NO_3), via the determination of the concentration of NH_4^+-N (QuikChem® method 31-107-06-1-I) and the concentration of NO_3-N (QuikChem® method 31-107-05-1-K) (cadmium reduction method). Seven matrix matched standards were used that spanned the range of analysis (5 – 500 µg L^{-1} for NH_4^+-N and NO_3-N). Each extraction was verified with an independent check standard. Precision was calculated as above and was ±3.2 %, ±1.8 % for NH_4^+-N and NO_3-N respectively. Accuracy was 0.9 % and 1.1 % for NH_4^+-N and NO_3-N analysis. Concentrations were corrected using the method blank (n = 4) to calculate final extract concentrations.

3.3.7 Data analysis

3.3.7.1 Statistical analysis

All statistical analysis was performed using R Core Team (2013). R: A language and environment for statistical computing. R foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org/.

3.3.7.2 Principal component analysis

Principal component analysis (PCA) was used to reduce the dimensionality of the dataset and enhance interpretation by creating new uncorrelated variables. PCA was run on R

Core Team (2013) using the prcomp package and visualised using the fviz_biplot package. We used standardised total element concentrations as the input variables for the 11 glacial flours, acting as the individuals. Data was standardised using Equation 14.

$$z = \frac{CTE_{glacier} - CTE_{mean}}{CTE_{standard\ deviation}} \qquad \text{(Equation 3.1)}$$

$CTE_{glacier}$ = *Concentration of trace element*
CTE_{mean} = *Mean concentration of trace element*
$CTE_{standard\ deviation}$ = *Standard deviation of trace element concentration*

In the cases where the total element concentration was less than the method detection limit, the method detection limit was used. Data was considered suitable for PCA analysis, where eigenvalues > 0.1 (Grossman, Nickerson, and Freeman 1991). Data was rotated using the inbuilt rotation method varimax within R. Using the results of the PCA we then used k-means cluster modelling, using the k-s package, to determine the best number of clusters within the 11 glacial flours. The best number of clusters had a significant proportion (~ 95 %) of the variance in the principal components (Xue et al. 2011).

3.4 Results

3.4.1 Macronutrients: N, P, K, Ca and Mg

As expected, Exchangeable N concentrations associated with the glacial flours from all glaciers investigated in this study were within one standard deviation of the method detection limit and therefore presumed insignificant. We found large differences in all measured P fractions between glacial flours of contrasting geologies, with much less variance for flours based on similar geologies (Table 3.3). (Porder and Ramachandran 2013). Based on glacial flour P-CR content and the underlying bedrock geology, the sequential P fraction concentrations show difference which relate to the Suchet rock classification (Amiotte Suchet, Probst, and Ludwig 2003). The latter differentiates metamorphic-sedimentary (Group 1) glaciers from mixed bedrock (metamorphic-sedimentary-igneous) (Group 2), igneous (mafic) (Group 3) and igneous-metamorphic (Group 4). The different rock types varied in P speciation.

Firstly, regarding Labile-P (Extraction 1), Group 2 and 3 glaciers had measurable MgCl-P which ranged from 0.72 – 14.4 µg g^{-1} and 2.76 – 10.38 µg g^{-1} respectively.

Approximately 10 – 20 % of the Labile-P in Group 2 and Group 3 glacial flours was held within the MgCl-P phase, whilst the remaining 80 – 90 % was held within the NaOH-P phase (Labile P Extraction 2). This differed considerably to both the Group 1 and Group 4 glacial flours, where 100 % of the Labile-P (Extraction 1 ($MgCl_2$) + Extraction 2 (NaOH)) was held within the NaOH-P, sorbed to Fe and Al minerals. Group 1 Labile-P ranged from 27.4 – 62.3 µg g^{-1} whilst Group 4 Labile-P ranged 5.3 – 57.6 µg g^{-1}. Group 1 and 4 glacial flours are known to contain reactive ferrihydrite particles that have the potential to precipitate P, and which are likely liberated within the NaOH-P extraction phase (Mitchell, Brown, and Fuge 2001; Pryer et al. 2020; Hawkings et al. 2014).

Secondly, the sequential P extraction data show that HCl-P (Extraction 3) was the dominant (> 95 %) P fraction within all uncrushed glacial flour, likely a reflection of P associated with apatite minerals (Table 3.2). This is further supported by a positive correlation ($R^2 = 0.56$, $p < 0.05$) of P-CR with Ca concentration in the flours (Table 3.3). Group 3 had the highest range in HCl-P concentration, 935 – 1315 µg g^{-1}, likely due to the major carbonate forming cations (Mg, Ca) that are known to comprise between 25 – 30 % (wt %) of the alkaline volcanic basalts that compose Sólheimajökull and Falljökull bedrocks (Schaef, McGrail, and Owen 2009).

Thirdly, total-P-NCR (Ext 4) concentrations were within the range of previous research upon glacial flour (Hodson, Mumford, and Lister 2004; Föllmi et al. 2009; Hawkings et al. 2016). Total glacial flour PNCR concentrations indicated that glaciers in Groups 1, 2 and 4 bedrock types had a similar range: Total-PNCR Group 1 = 404 – 997 µg g^{-1}; Group 2 = 672 – 1123 µg g^{-1}; and Group 4 = 643 – 914 µg g^{-1} (Table 3.3). However, Group 3 which includes Igneous (mafic) volcanic basalt glaciers had the highest range of Total-PNCR (949 – 1415 µg g^{-1}) due to the larger HCl-P phase.

Glacial flour Total-P-CR (ICP-MS total extraction) indicated the full P concentration of the different flours and showed that crushing alongside a more intensive reaction extracted a greater proportion of P for all flours. Group 1 metamorphic and sedimentary bedrocks had the lowest range in Total-P-CR, 715 – 1689 µg g^{-1}. Group 4 igneous-metamorphic granitic bedrock based glacial flours Total-P-CR ranged from 1594 – 1881 µg g^{-1}, the increase compared to the Total-PNCR is likely due to the increased breakdown of hard resistant silicate rock components. The mixed bedrocks in Group 2 had the second highest range of Total-PCR, 2220 – 2364 µg g^{-1}. Finally, Group 3, igneous (mafic) volcanic basalts had the highest range of Total-PCR 2810 – 2922 µg g^{-1}.

The glacial flour extraction for Total K also follow the groupings 1 – 4 based on bedrock type. Group 1 metamorphic and sedimentary bedrock glaciers displayed glacial flours with the highest concentration range of Total K, 5980 – 9100 µg g^{-1} (Table 3.4). Group 2 glaciers with mixed bedrock are divided, with Chhota Shigri (Total K 8410 ± 370 µg g^{-1}) aligning with the range of Group 1 glaciers, and Tirich Mir glacial flour (Total K 6080 ± 350 µg g^{-1}) being more like the igneous volcanic rocks in Group 3. The range of K concentrations within Group 3 were 5610 - 6960 µg g^{-1} with corresponded with high Total Ca concentrations (Falljökull 22800 ± 120 µg g^{-1}, Sólheimajökull 27400 ± 460 µg g^{-1}), as expected for mafic igneous rocks that are known to also contain high concentrations of Ca-rich plagioclase (albite, anorthite) (Smith and MacKenzie 1958; Jakobsson, Jónasson, and Sigurdsson 2008). Group 4 glaciers had much lower Total K, ranging from 1410 – 2550 µg g^{-1}, which was lower than expected for granitic based bedrock. These values suggest that the K in Group 4 glacial flour may be held in silicate fractions (e.g., quartz) that were more resistant to the extraction method used. However, although these figures may be an underestimate for Group 4 glacial flours, they act as an indicator of the poor K provision via these glacial flours if applied to agricultural soils. Our extraction dataset indicates that Group 1 - 3 glacial flours displayed an inverse relationship between Total P-CR and Total-K concentration ($r^2 = 0.61$, $p < 0.05$) (Figure 3.1).

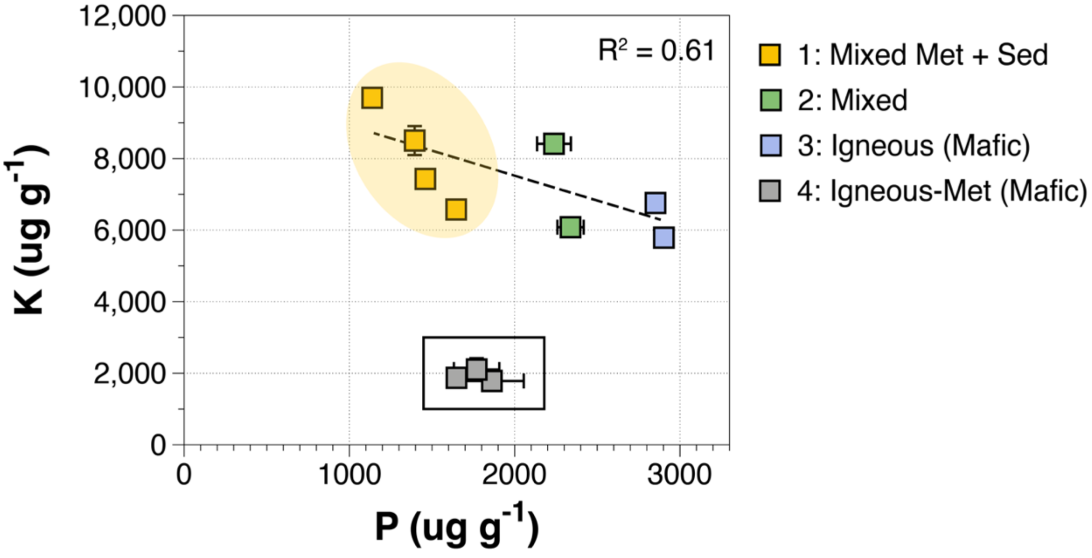


Figure 3.1: Potassium (K) and phosphorous (P) concentration (µg g^{-1}) of the glacial flours investigated. The black square indicates the three granitic bedrock glacial flours that potentially were not fully digested in the extraction and were not included in the regression analysis. R^2 for Groups 1:3 is shown.

Table 3.3: Sequential Phosphorous extraction results for 11 glacial flours. P-NCR = Total P uncrushed from sequential extraction using K_2SO_4. PCR= Total P crushed and extracted as a component of the Total metals extraction (HCl + HNO_3). Labile-P is combined $MgCl_2$-P + NaOH-P. Mean values are presented to 3 significant figures; the error is a measure of standard deviation. Values for n in brackets represent the replicates for P-CR if different to P-NCR. Values are also presented with previously reported glacial range for suspended particulate phosphorous from glacial meltwater for comparison.

Bedrock Group	**Glacier**	**$MgCl_2$-P**	**NaOH-P**	**HCl-P**	**Res-P**	**Total-P-NCR**	**Total-P-CR**	**Labile-P**	**n**
		(µg g^{-1} (Dry sediment))							
Group 1: Met-Sed	Arolla	-	35.8 ± 8.4	880 ± 65	13.4 ± 1.8	929 ± 68	1395 ± 35	35.8 ± 8.4	3
	Bara Shigri	-	46.7 ± 15.6	453 ± 71	10.8 ± 2.7	493 ± 89	1460 ± 25	46.7 ± 15.6	3
	Pastoruri*	-	-	-	-	-	737 ± 23	-	3
	Shallap*	-	-	-	-	-	1646 ± 43	-	3
Group 2: Mixed	Chotta Shigri	1.24 ± 0.52	4.35 ± 2.68	724 ± 52	3.07 ± 2.56	733 ± 61	2240 ± 10	5.59 ± 2.78	9 [3]
	Tirich Mir	10.9 ± 3.5	56.2 ± 10.1	951 ± 64	18.9 ± 5.1	1040 ± 83	2340 ± 24	67.1 ± 13.1	6 [3]
Group 3: Igneous (Mafic)	Falljökull	5.61 ± 2.85	21.6 ± 12.7	1020 ± 85	2.15 ± 0.78	1050 ± 101	2900 ± 22	27.2 ± 14.6	3
	Sólheimajökull	9.79 ± 0.61	79.2 ± 5.4	1235 ± 80	5.16 ± 2.08	1320 ± 95	2850 ± 40	89.0 ± 5.1	9 [3]
Group 4: Igneous-Met	Kiattut Sermiat	-	10.6 ± 5.3	811 ± 55	17.3 ± 7.8	840 ± 74	1860 ± 21	10.6 ± 5.3	3
	Leverett	-	12.5 ± 6.9	785 ± 47	26 ± 8.4	824 ± 68	1770 ± 18	12.5 ± 6.9	3
	Steffen	-	40.3 ± 17.3	722 ± 66	86.9 ± 22.3	730 ± 87	1650 ± 56	40.3 ± 17.3	10 [3]
Glacial range[†]		*0.1 – 4.8*	*0.9 – 52*	*95.3 – 1175*	*8.4 – 34*	*375 – 1209*		*1.0 - 52*	

*Pastoruri and Shallap glacier were not extracted for sequential phosphorous, but were investigated for Total-P-CR

[†] Glacial range is given from past studies Hawkings et al. (2016); Hodson, Mumford, and Lister (2004); Föllmi et al. (2009)

Table 3.4: Total Element concentrations for all investigated glacial flours. Values shown are the mean and standard deviation, n = 3. All values are shown to 3 significant figures. Global river suspended particulate material (SPM) mean (Martin and Meybeck 1979; Gaillardet, Viers, and Dupré 2003) and surficial rock mean (Rudnick et al. 2003; Rudnick and Gao 2014) also shown for comparison. Also presented are the permissible agricultural soil limits detrimental for plant toxicity in India and the EU (Singh et al. 2010; USEPA 2021)

		Al	**As**	**Ba**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**
Bedrock Group	**Glacier**	*(Total ($\mu g\ g^{-1}$))*							
Group 1: Met-Sed	Arolla	25700 ± 1300	4.86 ± 0.65	119 ± 12	13000 ± 600	< LOD	10.9 ± 0.5	20.5 ± 1.2	< LOD
	Bara Shigri	14100 ± 500	**36.9 ± 4.4**	86.8 ± 3.2	2580 ± 230	**1.89 ± 0.25**	7.38 ± 0.21	21.1 ± 0.6	< LOD
	Pastoruri*	19300 ± 750	13.0 ± 1.5	121 ± 5	1410 ± 100	**9.36 ± 1.75**	30.5 ± 1.89	6.78 ± 0.51	< LOD
	Shallap*	29900 ± 1100	**410 ± 12**	229 ± 11	4500 ± 230	< LOD	11.1 ± 0.8	26.4 ± 2.4	< LOD
Group 2: Mixed	Chotta Shigri	11300 ± 680	**73.8 ± 8.0**	30.2 ± 2.1	2350 ± 150	< LOD	5.79 ± 0.07	13.0 ± 0.2	< LOD
	Tirich Mir	19000 ± 680	2.43 ± 0.17	135 ± 8	7440 ± 180	< LOD	24.4 ± 1.95	**37.9 ± 2.6**	62.5 ± 3.4
Group 3: Igneous	Falljökull	60200 ± 680	2.56 ± 0.22	240 ± 9	22800 ± 120	< LOD	39.3 ± 0.4	12.6 ± 0.6	< LOD
	Sólheimajökull	65500 ± 2100	2.59 ± 0.03	235 ± 7	27400 ± 460	< LOD	70.3 ± 1.5	**33.7 ± 0.9**	< LOD
Group 4: Igneous-Met	Kiattut Sermiat	11700 ± 1100	1.55 ± 0.03	50.4 ± 5.5	5860 ± 390	< LOD	9.92 ± 1.30	**43.3 ± 6.5**	< LOD
	Leverett	10200 ± 940	1.85 ± 0.11	57.7 ± 6.9	5430 ± 190	< LOD	9.73 ± 1.56	**36.7 ± 2.5**	< LOD
	Steffen	13600 ± 340	2.08 ± 0.06	38.8 ± 1.1	5980 ± 70	< LOD	8.41 ± 0.02	24.5 ± 0.5	< LOD
River SPM Mean		*94000*	*5*	*600*	*21500*	*1*	*20*	*100*	*100*
Surficial Rock Mean		*69300*	*7.9*	*445*	*45000*	*0.2*	*13*	*71*	*32*
Indian standards 2010			**20**			**3 – 6**		**124**	**135 – 270**
US EPA standards 2021		**300,000**	**18**	**2000**		**0.36**	**130**	**34 - 130**	**49**

Table 3.4 (continued): Total Element concentrations for all investigated glacial flours. Values shown are the mean and standard deviation, n = 3. All values are shown to 3 significant figures. Global river suspended particulate material (SPM) mean (Martin and Meybeck 1979; Gaillardet, Viers, and Dupré 2003) and surficial rock mean (Rudnick et al. 2003; Rudnick and Gao 2014) also shown for comparison. Also presented are the permissible agricultural soil limits detrimental for plant toxicity in India and the EU (Singh et al. 2010; USEPA 2021)

		Fe	**K**	**Mg**	**Mn**	**Ni**	**Pb**
Bedrock Type	**Glacier**			*(Total ($\mu g\ g^{-1}$))*			
Group 1: Met-Sed	Arolla	29250 ± 1200	8500 ± 600	7970 ± 320	< LOD	18.2 ± 0.7	23.7 ± ± 2.3
	Bara Shigri	20200 ± 420	7430 ± 240	6930 ± 90	< LOD	17.9 ± 0.5	12.8 ± 1.2
	Pastoruri*	16980 ± 1700	8440 ± 500	2070 ± 600	**7770 ± 120**	**35.2 ± 0.8**	204.8 ± 2.8
	Shallap*	129800 ± 2600	6580 ± 600	9720 ± 400	690 ± 80	13.2 ± 1.1	73.0 ± 1.9
Group 2: Mixed	Chotta Shigri	20500 ± 320	8410 ± 370	3470 ± 90	< LOD	12.8 ± 0.2	8.70 ± 0.24
	Tirich Mir	64500 ± 1800	6080 ± 350	12800 ± 450	456 ± 62	31.8 ± 0.7	8.05 ± 0.45
Group 3: Igneous	Falljökull	117000 ± 900	5790 ± 180	18900 ± 500	1980 ± 50	21.1 ± 0.4	3.16 ± 0.12
	Sólheimajökull	153000 ± 3800	6760 ± 200	33500 ± 900	2500 ± 70	**86.9 ± 2.9**	3.71 ± 0.19
Group 4: Igneous-Met	Kiattut Sermiat	34300 ± 5500	1780 ± 370	5140 ± 430	690 ± 40	22.1 ± 2.2	3.17 ± 0.27
	Leverett	28600 ± 1100	2100 ± 450	4780 ± 380	< LOD	21.7 ± 1.5	3.93 ± 0.11
	Steffen	32500 ± 1200	1870 ± 50	5700 ± 150	< LOD	15.4 ± 0.4	7.46 ± 0.09
River SPM Mean		*48000*	*20000*	*11800*	*1050*	*90*	*150*
Surficial Rock Mean		*35900*	*24400*	*16400*	*720*	*49*	*16*
Indian standards 2000						**75 – 150**	**200 – 500**
US EPA standards 2021		**550,000**			**4000**	**38**	**120**

Table 3.4 (continued): Total Element concentrations for all investigated glacial flours. Values shown are the mean and standard deviation, n = 3. All values are shown to 3 significant figures. Global river suspended particulate material (SPM) mean (Martin and Meybeck 1979; Gaillardet, Viers, and Dupré 2003) and surficial rock mean (Rudnick et al. 2003; Rudnick and Gao 2014) also shown for comparison. Also presented are the permissible agricultural soil limits detrimental for plant toxicity in India and the EU (Singh et al. 2010; USEPA 2021)

Bedrock Type	**Glacier**	**S**	**Se**	**Si**	**Sr**	**Zn**
				(Total ($\mu g\ g^{-1}$))		
Group 1: Met-Sed	Arolla	2890 ± 490	**6.07 ± 0.61**	870 ± 79	270 ± 11	< LOD
	Bara Shigri	1940 ± 200	**3.13 ± 0.78**	934 ± 80	16.2 ± 1.1	< LOD
	Pastoruri*	3270 ± 180	**1.70 ± 0.22**	< LOD	28.9 ± 2.1	**984 ± 8**
	Shallap*	12500 ± 300	**2.29 ± 0.18**	781 ± 210	58.7 ± 7.4	185 ± 5
Group 2: Mixed	Chotta Shigri	1130 ± 150	**3.50 ± 0.49**	1020 ± 170	< LOD	114 ± 3
	Tirich Mir	1760 ± 240	**3.14 ± 0.74**	535 ± 30	202 ± 80	125 ± 6
Group 3: Igneous	Falljökull	2500 ± 170	**5.41 ± 0.57**	635 ± 59	296 ± 5	190 ± 3
	Sólheimajökull	3560 ± 70	**6.01 ± 0.25**	< LOD	**444 ± 15**	232 ± 2
Group 4: Igneous-Met	Kiattut Sermiat	< LOD	**2.37 ± 0.82**	1160 ± 120	37.7 ± 4.0	< LOD
	Leverett	< LOD	**1.71 ± 0.13**	1170 ± 20	33.8 ± 0.5	< LOD
	Steffen	< LOD	**2.43 ± 0.31**	676 ± 51	73.7 ± 2.1	< LOD
River SPM Mean		*6000*	*7.0×10^{-11}*	*285000*	*150*	*350*
Surficial Rock Mean		*1250*	*0.05*	*362000*	*278*	*127*
Indian standard 2000			**10**			**300 – 600**
US EPA standards 2021			**0.63**		**465**	**250**

3.4.2 Trace element concentration PCA

Glacial flours showed significant variation in TE concentrations, however the bedrock groups 1 – 4 clustered together in the PCA analysis of TE concentrations (Figure 3.2). Thus, the PCA analysis performed on the TE extraction dataset supports the bedrock control on TE content. The PCA indicated that 92.4 % of the glacial flour total element concentration variance was explained by the first 5 principal components (PC) with eigenvalues > 1. Cumulatively, PC1 + PC2 accounted for 66.4 % of the variation and can be visualised in the PCA biplot (Figure 3.2). PC1 and PC2 were controlled by a combination of TE typically associated with rock type. PC3, was dominated by Total Cu content (89 %) which was measured in only Tirich Mir glacier, all other glaciers < LOD. PC4 and PC5 were controlled by Pb and As respectively.

PC1 explained 51.3 % of the total variance within the dataset, the top contributing positive variables were Mg (8.8 %), Na (8.8 %), Co (8.8 %), Fe (8.5 %), Mn (8.3 %), Al (8.1 %) and Ca (8.0 %) – mafic components. Within PC1, Si had a strong negative coordinate (-0.75) and a contribution of (5.2 %), which reflects the mafic component in the bedrock. Group 3 glacial flours from igneous mafic bedrocks were the most dominant in PC1, Sólheimajökull glacial flour was the dominant individual contributing 52.5 % of variance whilst Falljökull contributed 19.6 % of the variance. Group 3 glaciers were the richest in TE known to be beneficial for plants (e.g., Fe, Zn, Mn, Ni and Sr) whilst Group 1 glaciers have the lowest concentrations of these TE.

The second component most responsible for TE variation was PC2 (the y-axis in Figure 3.2). PC2 had positive associations with the variables Pb (28.2 %), As (26.3 %), S (23.0 %) K (8.5 %). However, PC2 had weaker negative loadings for Cr (-0.25), P (-0.23) and Ni (-0.23) that contribute less to the variation (Cr 2.1 %, P 1.7 %, Ni 1.7 %). The TE that displayed positive associations with PC2 are common sedimentary rock TE, whilst the TE with weak negative are common silicate rock TEs. Therefore, PC2 was likely an indicator of sedimentary rock, specifically, sulphide content, a common component in metamorphic and sedimentary bedrock this is because of two reasons. The individuals most responsible for PC2 were Shallap glacial flour (65.7 %) and secondly, Pastoruri glacial flour (4.7 %) known to be rich in metal-sulphides and sedimentary rock.

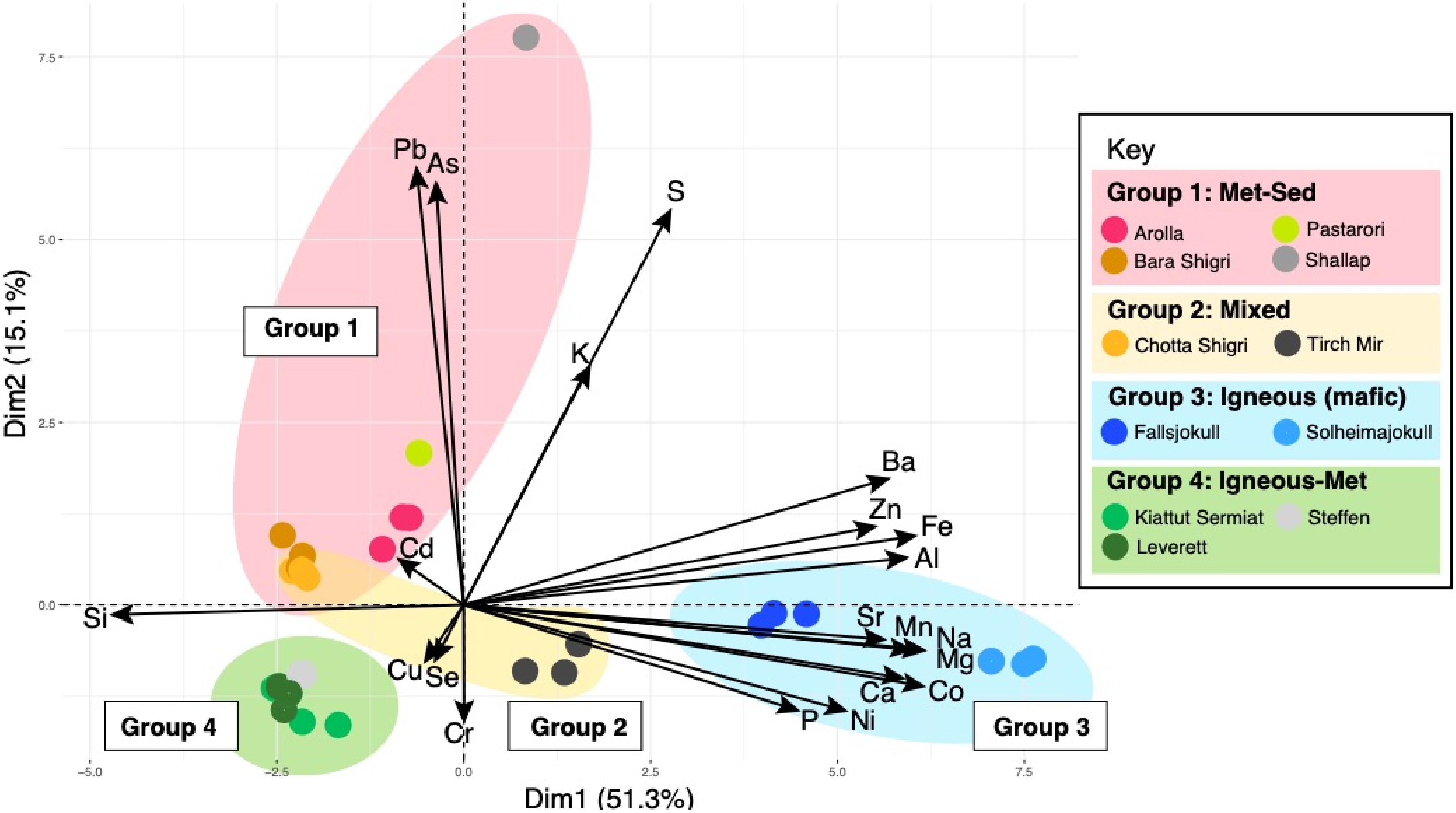


Figure 3.2: PCA Biplot of Principal component 1 (51.3 %) and principal component 2 (15.1 %). Showing all glacial flours as individuals and elemental concentration as variables. Glacial flours group based on bedrock type. Mixed bedrocks (Group 2) are split with overlap in Group 1 Chhota Shigri whilst Tirich Mir is clustering towards Group 3, Igneous-Met.

Group 4 glacial flours, the Igneous-Metamorphic flours that were composed of granitic bedrock plotted closely together on the PCA (Figure 3.2). The PCA analysis also indicated which bedrock type may be more dominant beneath the mixed bedrock of Group 2 glaciers (Figure 3.2). Chhota Shigri glacier in Group 2 clustered closer with Group 1, although Chhota Shigri flour did have some granitic bedrock, the TE appeared more aligned with Group 1. This was likely due to the metamorphic gneiss and sulphide rich sedimentary black shales. Tirich Mir glacier in Group 2 was also of mixed bedrock with igneous, metamorphic, and sedimentary components, and was central to all glacial flour groups on the PCA.

3.5 Discussion

3.5.1 Macronutrient supply from glacial flour

3.5.1.1 Phosphorous

This dataset further confirms the findings of past research that inferred that glacial flour acts as a source of Labile-P (Hawkings et al. 2016; Hodson, Mumford, and Lister 2004; Föllmi et al. 2009), which is an essential macronutrient for plant growth. Similar to past studies, the majority of P in glacial flour is held with the HCl-bound fraction which includes minerals, such as apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) (Hawkings et al. 2016). This has the potential to be liberated via chemical dissolution through chemical and biological rock weathering (Lucas 2001; Drever 1994; Bland and Rolls 1998). Phosphate mineral diversity in igneous and metamorphic rocks is dominated by apatite (Nash 1984).

Apatite in igneous rocks is commonly an accessory mineral and its abundance tends to decline with increasing silica content (Koritnig 1978), which likely explains why Sólheimajökull flour rich in alkaline mafic basalts (lower silica) had a much higher P content than the Greenlandic glacial flours (high silica) shield rocks (Amiotte Suchet, Probst, and Ludwig 2003). Within the igneous rocks studied, P increased from silica-rich granitic shield rocks (Group 4: Igneous+Met Leverett, Kiattut Sermiat and Steffen), to mafic basaltic rocks (Group 3: Igneous (Mafic) Sólheimajökull and Falljökull). The results from the series of P extractions on a variety of glacial flours indicate that glaciers overlying alkaline basalts (e.g., Sólheimajökull) may potentially be the best source of P for agriculture.

P is relatively immobile during metamorphism, therefore the P content of metamorphic rocks reflects the abundance in the unmetamorphosed precursors (Porder and Ramachandran 2013). The difference in P concentration between Group 1 Bara Shigri and Chhota Shigri within the initial grouping of rock types likely reflects gneiss and chalcopyrite-bearing rocks beneath Chhota Shigri from the High Himalayan Crystalline Sequence that are lacking beneath Bara Shigri from the Tethys Himalaya Sequence (Kumar and Dobhal 1997; Azam et al. 2019). Interestingly, the P content of glacial flour decreased as sedimentary bedrock constituents increased, which is likely due to the influence that increasing sedimentary grain size exerts on limiting P crystallisation (Holtan, Kamp-Nielsen, and Stuanes 1988). The results show that glacial flour composed of mixed metamorphic rock, such as Chhota Shigri glacial flour has the highest potential to act as a source of P for crops.

3.5.1.2 Potassium

The K content of glacial flours is dependent on the underlying bedrock geology. Glacial flours rich in K such as Arolla and Shallap reflect the likely presence of K-containing minerals such as feldspars and muscovite compared to the basaltic mafic rocks of Sólheimajökull (Table 3.3). The granitic Group 4 glacial flours had the lowest K content compared to the other glacial flours studied, likely due to the common occurrence of K-depleted tholeiites present in these strong silicate rocks (Anhaeusser et al. 1969). The Total K content of all assessed glacial flours were an order of magnitude lower than the average surficial rock K content (25,500 ug g^{-1}), which may be due to the incomplete decomposition of the most resistant silicate structures from the aqua regia digest compared to more intensive digestions using hydrofluoric acid, leading to an under reporting of K content in this study (Martin and Meybeck 1979).

The results from this study indicate that glacial flour may have potential within agriculture as a source of K, acting as an alternative source of crushed silicates (Manning 2010). However, the negative relationship between K and P-CR (Figure 3.1) suggests that glacial flours suitable for enriching soils in both nutrients are the mixed bedrock glaciers, Group 3, Chhota Shigri and Tirich Mir. These two glaciers are composed of mixed igneous-metamorphic-sedimentary bedrock and are therefore potentially able to provide both essential macronutrients through rock weathering within the soil. However, the chemical dissolution of carbonate, silicate and sulphide minerals is also likely to release both beneficial and toxic TE.

3.5.2 Trace elements

Glacial flour also has potential to act as a source of trace elements, but the balance between TMs which can be beneficial nutrients versus sources of toxic species is critical and depends on the abundance of mineral sulphides in the bedrock. Sulphide oxidation coupled with carbonate dissolution is often the dominant reaction in proglacial landscapes (Wadham et al. 2007). Glacial flours with concentrations of TE (As, Cd, Cr, Mn, Ni, Pb, Se, Sr and Zn) above soil standards (Indian standards 2010, US EPA 2021) are particularly concerning for agricultural regions either on recently deglaciated terrain or downstream of glaciers and relying on glacial meltwater for irrigation such as the Himalayas and the Andes (Table 3). Shallap glacier has very high S concentration (12,500 ± 300 ug g^{-1}) compared to all other studied glaciers, and the river SPM mean (6000 ug g^{-1}) and surficial rock mean (1250 ug g^{-1}). Its proglacial river is known to release high concentrations of toxic TMs and acidity to downstream environments (Table 3) (Grande et al. 2019). The results of our PCA indicate that bedrocks with underlying sulphide components, such as Shallap, have the potential to release As, Cd, Pb. However, when applied in low doses as part of a composting soil mixture (< 0.01 T ha^{-1}) such as bokashi, even potentially toxic glacial flours could provide a beneficial source of TE without becoming toxic e.g. low dose Himalaya flour may not result in As toxicity (Singh and Ramanathan 2018). Glacial flours such as Shallap, have multiple elements at high toxicity levels, potentially resulting in multi-element toxicity (Nagajyoti, Lee, and Sreekanth 2010; Goldhaber 2003). The risk of enriching soils with toxic elements is not isolated to glacial flour, but all crushed rock soil amendment strategies, highlighting a need to assess TE levels prior to use (Beerling et al. 2018a).

3.5.3 Beneficial TE supply from glacial flour

Our results show that all glacial flours contained beneficial micronutrients and thus had the potential to release beneficial TE concentrations (Fe, Mn, Cu, Zn, Ni, Mo, Se and Co) (Table 3). TE that are commonly lacking in human diets (Cu, Se and Zn) are particularly difficult to manage within the soil-plant food system, yet our results show that glacial flours sourced from Group 2 or 3 (Mixed or Igneous mafic) bedrocks, e.g. Sólheimajökull or Tirich Mir can be rich in these TE (White and Broadley 2009). These beneficial TE are usually associated with Mg and Fe rich mafic rocks and therefore these bedrocks form the ideal source for beneficial glacial flours (Wang et al. 2021). The results of this glacial flour nutrient content dataset indicate that mineral rich basalt rock, such as Sólheimajökull, provides the highest quantity of all beneficial TE.

3.6 Conclusion

This study has shown that glacial flours have potential to act as a source of beneficial macro and micronutrients for agriculture. Basaltic rock (e.g., Sólheimajökull glacier) is richest in beneficial nutrients and may act as a clear indicator of the full potential of glacial flour treatment. However, glacial flours rich in toxic TE, such as Shallap and Chhota Shigri glacier, are concerning and may require future remediation strategies. We have shown the importance of analysing glacial flour TE content prior to inclusion as a soil treatment to avoid toxic components. The next steps to assess glacial flour as a potential soil treatment involve an assessment on crop yield and the nutritional value of crops.

Chapter 4.

Glacier to grain; glacial flour as a soil fertility treatment in mountain regions

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This paper has been prepared as a research article for future submission to Nature Geoscience in June 2022, with the following reference,

Tingey ST[1], Wadham JL,[1,2], Telling J[3], Flynn S[3], Hawkings JR[4], Yates CA[5], Lamarche-Gagnon G[1], Ramanathan AL[6], Hetherington A[7], Dodd AN[8], Sgouridis F[1]. Glacier to grain; glacial flour as a soil fertility treatment in mountain regions. *Nature Geoscience.* (2022)

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4.1 Abstract

The challenge of meeting the food production demands of a growing global population, whilst increasing sustainability, could be moderated by the adoption of novel crop cultivation strategies that improve the bioavailability of soil nutrients and enhance crop nutrition. A widely proposed method of biogeochemically enhancing soils is the addition of crushed rock to agricultural land. However, cost effective, sustainable production methods remain an obstacle. Here, this thesis proposes naturally crushed rock produced by glaciers, "glacial flour", known to rich in nutrients (P, K, Fe and micronutrients), as an accessible alternative to mechanically-crushed material. This study is the first controlled laboratory crop growth investigation of soybean (*Glycine max*. var. Black jet) with glacial flour, sourced from a Himalayan glaciated catchment with gneiss bedrock and Icelandic basaltic catchment. The results demonstrated that these glacial flours successfully enhanced crop yields by 85 % and 135 % respectively compared with controls. The application of glacial flour also substantially boosted the nutritional content of the crop in important elements for human health 'by biofortification' (e.g., Zn, Se). However, glacial flour from the Himalayas also resulted in the bioaccumulation of the toxic heavy metal, As. These results highlight the need for geological screening prior to incorporation within farming practices. Overall, this investigation indicates that glacial flour has the potential to act as a novel soil remediation strategy for sustainable agriculture.

4.2 Introduction

Agriculture in the 21st century faces a global food production challenge if it is to meet the needs of a predicted world population of 9 billion by 2050 in a sustainable way (United Nations 2017). This will require investment in small holder practices and a global shift towards sustainability within intensive agriculture, whilst ensuring nutritious produce (Manning 2010; Altieri, Nicholls, and Montalba 2017; DeLonge, Miles, and Carlisle 2016). One potential method of rejuvenating soils and improving productivity is the application of fresh mineral material (Hensel 1894a), such as crushed rock. Existing studies have shown that crushed rock acts as a source of phosphorus (P), potassium (K), and micro-nutrients (iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn)) for crops, enhancing crop yields by up to 60 % (Bakken et al. 2000; Beerling et al. 2018a; Priyono and Gilkes 2008b; Ramos, de Mello, and Kautzmann 2014; Gillman 1980; Coroneos, Hinsinger, and Gilkes 1996), whilst enhancing plant health, water retention and soil CO_2 sequestration (Moosdorf, Renforth, and Hartmann 2014; Edwards et al. 2017; Hartmann, West, Renforth, Kohler, et al. 2013; Kantola et al. 2017; Beerling et al. 2018a). However, the impact of crushed rock on crop growth within typical agricultural soils is highly constrained by its mineralogical composition and particle size, in addition to consideration of its chemical interaction with an agricultural soil (Beerling et al. 2018b; Priyono and Gilkes 2008b). A drawback in the adoption of crushed rock to improve soil fertility is also the need to selectively mill rocks of desired mineralogical properties or to source substantial amounts of pre-milled material, both of which have a non-trivial carbon footprint and high economic costs (Priyono and Gilkes 2008b; Beerling et al. 2020; Beerling et al. 2018b; Blanc-Betes et al. 2020).

A novel and promising alternative to the application of mechanically-crushed rocks is to employ material which has been naturally crushed by erosional agents, one of the most powerful of which are glaciers. Glaciers are 'sediment factories', efficiently eroding and crushing their underlying bedrock to fine (silt/clay sized < 63 µm) highly reactive particles, hereafter referred to as 'glacial flour' (Brown, Tranter, and Sharp 1996b). There are four potential benefits of using glacial flour as a soil fertility treatment. First, there is considerable evidence that glacial flour is rich in potentially bioavailable nutrients (P, Fe, micronutrients), and could therefore act as a nutrient source for crop growth and nutritional enhancement (biofortification) (Hawkings et al. 2016; Hawkings, Skidmore, Wadham, Priscu, Morton, Hatton, Gardner, Kohler, Stibal, and Bagshaw 2020; Hawkings et al. 2017; Hawkings et al. 2015a; Hawkings et al. 2014; Nienow et al. 2017). Second, high quantities of glacial flour are released from beneath glaciers and transported downstream by rivers every year. Concentrations of up to 0.5 $g\ L^{-1}$ are observed during peak summer discharge in mountainous valley glacier-fed rivers, such as Chhota Shigri glacier, North West Indian Himalaya, which has an estimated average annual sediment yield of 1689 $T\ km^{-2}\ year^{-1}$(Singh, Ramanathan, and Pottakkal 2016a). This material is deposited and available from riverbanks, lake shores and in reservoirs (Cowton et al. 2012; Singh et al. 2015). Third, climate change and increased water scarcity have led to widespread investment in water management measures across mountainous glacially covered regions, like the Himalayas (Grumbine and Pandit 2013).

One measure to exploit glacially-fed watercourses, the construction of hydroelectric dams, combines the need to store valuable water in reservoirs with generating renewable energy. For these reasons, hydroelectric dams are being constructed in mountainous regions at a rapid rate. Dams are highly effective sediment traps and prevent the transport beneficial particulate nutrients to downstream ecosystems (Maavara et al. 2020). Rather than removal and or flushing, there is potential for recovery of these glacier-derived dam sediments to provide a sustainable source of nutrients for agriculture in regions within proximity to dams. Finally, in certain populous regions of the world, there is an intersection between glacier coverage and substantial and widespread food security issues, the Hindu-Kush Himalaya being an example (Houlton, Morford, and Dahlgren 2018).

This study will assess the potential of two geologically contrasting glacial flours to improve soil fertility and enhance the yields, growth, and nutritional content of the widely cultivated legume, soybean (*Glycine max.* var. Black jet), in the first controlled glasshouse investigation using glacial flour harvested from mountain glaciers. The legume soybean was selected to eliminate the need for nitrogen (N) fertilisation since it fixes nitrogen through rhizobia in its root nodules (Wadham et al. 2016). Despite some sedimentary bedrocks being N-rich, it is unlikely that rock N concentrations transfer directly to plant N input (Houlton, Morford, and Dahlgren 2018). The research presented in Chapter 3 also found that glacial flour Exchangeable inorganic N (plant available) was unsignificant. Soybeans are one of the most valuable, widely cultivated global crops: they are important as an oil seed; a component of human diets; and are used as biofuels and feedstocks (Masuda and Goldsmith 2009). Our two glacial flours of contrasting geologic origins are: (i) Icelandic glacial flour, from Sólheimajökull glacier, Iceland (63.4 °N, 19.4 °W) and originating from flood basaltic terrain, a geological type previously highlighted as having potential for crop fertilisation and carbon capture via enhanced weathering (Beerling et al. 2018b; Sigmarsson and Steinthórsson 2007); and (ii) Himalayan glacial flour, from Chhota Shigri glacier, India (32.3 °N, 77.7 °E), composed of igneous / metamorphic gneiss and granites with minor sedimentary bands (Kumar and Dobhal 1997). Himalayan glacial flour was chosen because of its potential for application via sustainable agricultural soil fertility solutions in a region of rising food demands (Mukherji et al. 2019; Nüsser et al. 2019; Wester et al. 2019). These results document the response of crop yield, plant health and nutrition following the addition of glacial flour to a low-nutrient soil matrix, in comparison to controls (no treatment) and traditional chemical fertiliser addition experiments (Maxwell and Johnson 2000). Overall, the results provide compelling evidence for the potential of glacial flour as a novel soil treatment in glacier-covered regions.

4.3 Methods

4.3.1 Glacial flour sites and sampling

Glacial flour was collected from two glacier field sites - see Supplementary Table 1 for glacial features. 'Iceland flour' was collected from Sólheimajökull, Iceland (63.4 °N, 19.4 °W) at the end of the ablation season in October 2016. Sólheimajökull is a well-documented land terminating outlet glacier of the Mydralsjökull ice cap, lying above the Katla volcanic system. Sólheimajökull bedrock comprises young (< 0.7 M yrs) volcanic basalts, known to contain quantities of elements such as K, P, Fe, Mn, Co, Ni, Mg, Ca as well as an array of rare earth elements (Sigmarsson and Steinthórsson 2007; Wood 1978; Larsen, Dugmore, and Newton 1999). 'Himalayan flour' was collected from Chhota Shigri (32.3 °N, 77.7 °E), a typical low latitude Himalayan glacier in the Chandra Bhaga river basin of the Lahaul and Spiti Valley, Pir Panjal range, Hindu Kush Himalayas, NW India at the end of the ablation season in September 2017 (Azam et al. 2012). Chhota Shigri bedrock is dominated by Rohtang gneisses - granite, with some chalcopyrite (Kumar and Dobhal 1997). All sediments were sampled from banks as close to the glacial portal as possible by the meltwater stream using sterilised trowels, into Whirl-Pak® bags where they were transported and stored in a fridge (~ 2 – 4 °C) until analysis and crop growth investigations.

4.3.2 Soil and Sediment analytical methods

4.3.2.1 Particle size

Particle size was determined using a Malvern Mastersizer 3000 analyser, which uses ultrasound to ensure sediment is broken down into its constituent particles, calculated based on five replicates. Sediment was suspended in MQ and then run through the Mastersizer to determine particle size distribution.

4.3.2.2 Nitrogen concentration determination

In the lab sediment exchangeable total nitrogen (Ex-N), comprising nitrate (NO_3^--N) and ammonia (NH_4^+-N) were determined as per Telling et al. (2011), but with a 2M KCl solution as per Maynard, Kalra, and Crumbaugh (1993). Extractions were filtered prior to analysis (0.45 µm 25 mm Whatman® GD/XP PES filters). Extract NO_3^--N and NH_4^+-N concentrations were determined colorimetrically using a flow injection analyser (LaChat QuikChem 8500 Series 2 FIA system, Loveland, CO, US), using QuikChem methods 31-107-06-1-I (NH_4^+-N) and 31-107-05-1-K (NO_3^--N). Precision for NO_3-N was ±1.8 % (n = 12) and accuracy was +1.1 %, based on six replicate matrix matched standards, spanning 1, 5, 10, 25, 50, 100, 250 and 500 ug L^{-1} NO_3-N. Precision for NH_4^+-N was ± 3.2 % (n = 12) and accuracy was ± 0.9 %, based on six replicate matrix matched standards, spanning 1, 5, 10, 25, 50, 100, 250 and 500 ug L^{-1} NH_4^+-N. The detection limits for NH_4^+-N and NO_3-N were 0.12 and 0.09 µg g^{-1} respectively for dry sediment.

4.3.2.3 Metal extractions (P, K, Fe, Ca, Mg, Mn, S, Se, Zn)

Phosphorous was sequentially extracted using the methods from Stibal et al. (2008) and Hawkings et al. (2016). This sequential extraction method removes decreasingly reactive operationally defined fractions of P. Extraction 1 removes loosely sorbed P using a 1 M $MgCl_2$ solution. Extraction 2 uses 0.1 M NaOH to removes Fe– and Al–bound P that is believed to be potentially biolabile (NaOH-P), with the sum of these two fractions termed 'Exchangeable P'. Extraction 3 removes Ca- and Mg- bound P, apatite bound P, which is less reactive using HCl (HCl-P). The final extraction, extraction 4, removes 'residual' and organic bound P (Res-P) using a potassium persulfate / sulfuric acid digest. Soluble reactive phosphorus concentrations in the resulting extracts were determined colourimetrically on a LaChat QuikChem® 8500 series 2 flow injection analyser (QuikChem method 31-115-01-1-I). At least 50 mg of sediment was added to the extraction solution (1.5 mL), each sequential extract was filtered (0.45 µm 25 mm Whatman® GD/XP PES filters) and then the sediment was washed with 2 mL of MQ which was filtered as above and added to the extract filtrate (dilution factor (d.f) x2). Each sequential filtrate was diluted prior to FIA analysis, with dilution factors as follows, extraction 1 d.f. x2, extraction 2 d.f. x5, extraction 3 d.f. x50. Precision was ±0.5 %, ±0.4 %, ± 0.2 % and accuracy was -0.5 %, +0.3 %, +1.4 % based on six replicate standards for extractions 1, 2, 3. Standards used were matrix matched and concentrations spanned 1, 5, 10, 25, 50, 100, 250 and 500 ug L^{-1} PO_4-P^-. Standards were checked by independent reference check standards (50 and 500 ug L^{-1} PO_4-P^-).

Labile metals (K, Fe) were determined using a sequential extraction method adapted from Tessier, Campbell, and Bisson (1979a). All equipment was cleaned using trace metal clean protocols, 24 hours in decon 80, 48 hours in 25 % v/v HCl and finally 24 hours in 25 % v/v HNO3 solutions, with 6 times MQ rinse inbetween each wash. Extraction 1 removes loosely-sorbed metals using a 0.5 M $MgCl_2$ solution. Extraction 2 removes metals bound to carbonates using a 1 M sodium acetate (NaOAc) solution. At least 100 mg of sediment was added to the extraction solution (1.5 mL), each sequential extract was filtered (0.45 µm 25 mm Whatman® GD/XP PES filters) and then the sediment was washed with 2 mL of MQ which was filtered as above and added to the extract filtrate (dilution factor (d.f) x2). Filters were acid washed using 20 mL 0.01M HCl followed by 30 mL MQ before drying in a trace metal clean laminar flow. The combination of both extraction 1 (e.g., MgCl-K) and extraction 2 (e.g., NaOAc-K) are termed 'exchangeable metals. Metal concentrations of the extracts were determined on an Agilent 710 ICP-OES. All extraction solutions were diluted by a d.f. x100 in 0.1M HNO_3 before running on the ICP-OES. Precision was ±0.8 %, ±0.5 %, ± 1.3 %, ±3.2 and accuracy was +2.2 %, +1.6 %, +2.8 %, -2.4 based on six replicate matrix matched standards for extractions 1, 2. Matrix matched standards for all element concentrations ranged from the 0.1 M HNO_3 blank (0), 1 5, 10, 25, 50, 100, 250 ug L^{-1}.

Total metals (P, K, Fe, Ca, Mg, Mn, S, Se, Zn, As) were determined on an Agilent 7500 inductive coupled plasma mass spectrometer ICP-MS after microwave digestion of sediments. For the microwave extraction, sediments were digested in a modified aqua regia solution for which all reagents were trace metal grade. For each digestion, 2 mL of 30% hydrogen peroxide, 2.5 mL 37% hydrochloric acid and 10 ml of 67% nitric acid was added to 0.1 – 0.5 g of sample. Digestions were carried out in pressurized Teflon vessels using a Mars 6 microwave. For each digestion, the temperature was ramped for 20 min to 210° C, where it was held for 15 min. After dilution samples were filtered through Whatman grade 41 filter papers and then diluted to 50 mL before analysis. To determine metal concentrations in the extraction solution an Agilent 7500 ICP-MS was used. The ICP-MS was configured with a micromist nebulizer, a cooled double concentric spray chamber and nickel cones. During analysis drift was monitored and corrected for using a 50 ppb In internal standard added to each sample using a T-junction inline mixing kit. Polyatomic interferences were removed using a collision-reaction cell with He gas. Precision for each element was P ±2.6 %, K ±2.9 %, Fe ± 0.8 %, Ca ±5.9 %, Mg ±2.6 %, Mn ±2.2 %, S ±9.1 %, Se ±1.9 %, Zn ±1.9 %, As ±2.2 %. Accuracy for each element was as follows P +0.2 %, K +2.5 %, Fe +1.1 %, Ca +0.4 %, Mg +3.8 %, Mn +0.7 %, S +4.1 %, Se +11.1 %, Zn +6.6 %, As +6.7 %, based on 6 replicate matrix matched standards covering the range of concentrations.

4.3.3 Crop yield experiments

4.3.3.1 Soybean plant material and growth conditions

Soybean (*Glycine max*) 'Black jet' seeds were stratified for 3 days at 4 ºC, then sown into vermiculite bags and propagated at 25 ºC, 100 % humidity until chitting was visible (5 - 8 days). Each germinated seed was then rolled in a microbial inoculum (*Bradyhizobium japonicum*) carried by peat to achieve root nodule formation and simulate a natural soil microbial ecosystem (source: LegumeFix, UK). The germinated beans were then planted into their treatments and artificial soils. Artificial soil was prepared using a volume to volume ratio of 9:1 perlite : commercial seedling compost (Silver Sand, Melcourt and Levingtons Seedling Compost) (Mohammed et al. 2014). Expanded perlite (Silvaperl P35 Grade, Hoben International, Westland Horticulture, UK) is an inorganic, relatively chemically inert, ultra-lightweight amorphous volcanic glass, with high water holding capacity and sufficient pore space to enable soybean root growth (ten Berge et al. 2012). Pots were 9 cm high, with 64 cm^2 surface area, each containing approximately 75 g of artificial soil. All materials were chosen for their low nutrient content comparable with most other plant growth matrixes to minimise external variables.

Prior to planting, artificial soils were mixed and specific treatment components were applied. Briefly, these were as follows; both glacial flours were applied at 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 T ha^{-1} equivalents which have been determined as the most application crushed rock application rates (Bakken et al. 2000). Fertilisers were applied at the follow rates; Chemical N at 10 kg ha^{-1}, Chemical P at 10 kg ha^{-1} and Chemical K at 10 kg ha^{-1}. Chemical N fertiliser addition was achieved through the application of Ammonium nitrate, NH_4NO_3, chemical P through P_2O_5 and chemical K through K_2O, all reagents were analytical grade with <0.5ppm heavy metals. Treatment pots were left to equilibrate for 7 days in a growth chamber before seedlings were transplanted.

Soybean plants were grown in a controlled environment (GroDome chambers; Unigro) with a 12:12 hour light: dark photoperiod at 50 % humidity, 20 ºC, and sunlight supplemented by 80 W m^{-2} overhead lighting supplied by <206 W Attis7 LED grow lamps. All soybean experiments occurred in winter (Nov – March 2018), ensuring consistent light levels. Plants were watered by hand daily with RO water to maintain optimal moisture conditions but minimise nutrient contamination. To reduce nutrient leaching, pots were placed in individual trays which were topped up with water. Once every 7 days 100 mL of RO water was added to the top of the pot around the plant as per Mohammed et al. (2014). For all experiments, at least four completely independent experimental repeats were performed per treatment, with 3 replicate plants within each of the experimental repeats, equating to 12 plants per treatment. At the end of the experiment post-harvest, all plants were recovered from the soils and root nodules were counted as an indicator of microbial soil health and nutrient availability (Mohammed et al. 2014).

4.3.3.2 Chlorophyll fluorescence imaging

Chlorophyll fluorescence imaging during the plant growth experiment was used to evaluate plant photosynthetic activity. The first fully expanded leaf from the top of the plant was analysed using chlorophyll fluorescence imaging to measure the photosynthetic efficiency of Photosystem II (PSII) at 2, 7, 12, 17, 22 and 27 days from the start of the experiment. Measurements occurred at a leaf temperature of 20 ºC. Prior to analysis, plants were dark-adapted in a completely dark chamber for 30 minutes. Chlorophyll fluorescence was measured using a pulse modulated fluorimeter (IMAGING-PAM M-Series Mini Walz). Fv/Fm scores are the most common method for measuring many types of plant stress, and helps determine the functioning capacity of photosystem II, the first protein complex in the light dependent reactions of photosynthesis (Maxwell and Johnson 2000). Fv/Fm test compares the minimum fluorescence (Fo) to maximum fluorescence (Fm). The fewer reaction centres available, the greater the plant stress. The difference between Fo and Fm is Fv, variable fluorescence. Fv/Fm is a normalised ratio that reports the maximum potential quantum efficiency of photosystem II if all available photosynthetic reaction centres were open. Fv/Fm was measured from four separate regions of interest on the lead that was selected for measurement. The % change in Fv/Fm was calculated compared to the day 0 score for that plant, the day the seedling was transplanted into the soils. Fv/Fm does involve measurements on different leaves over time acting as an indicator of physiological function.

4.3.3.3 Bean metal concentrations

Following crop growth experiments the plant material was extracted and analysed as per sediments using microwave digestion and ICP-MS quantification as above (Newcastle University).

4.3.4 Agricultural calculations

At the end of the experiment (50 days), plants were harvested, dried for 7 days at 65 ºC and separated to record biomass. Crop yield (g m^2) was calculated using the agricultural standard yield estimation for soybeans, Equation 1. Soybean yields were calculated for each separate experiment run consisting of a minimum of 4 replicates.

$$\frac{[\text{Pods m}^{-2}] \times [\text{no.of seeds per pod}]}{[100 \times \text{seed weight } (g)]} \qquad \text{(Equation 4.1)}$$

Agronomic efficiency (AE) calculations using crop yield were used to assess efficacy of treatments. Here, Y = yield of harvester portion of crop with nutrient applied, Y_0 = yield with no nutrient applied, F = amount of nutrient applied (Devasenapathy 2008; Dobermann 2007).

$$AE = (Y-Y_0) / F \qquad \text{(Equation 4.2)}$$

Enrichment factors (EF) for treatments were determined following the plant material analysis for metal content, indicating the transfer of metals from treatment to crop (Kisku, Barman, and Bhargava 2000). M_0 = Metal concentration in no treatment control. M_x = Metal concentration in treatment of interest. Where the no treatment control was below detection of the ICP-MS extraction method, the calculation was determined using the method limit of detection.

$$EF = M_0 / M_x \qquad \text{(Equation 4.3)}$$

4.3.5 Statistical analysis

All statistical analysis was performed using R Core Team (2013). R: A language and environment for statistical computing. R foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org/. Patterns of yield, nodules, Fv/Fm parameters were tested using a combination of the coefficient of determination (R^2) values, further supported using a test for significance, a p value < 0.05 is determined significant. This combination approach was used to increase confidence and to avoid inclusions of correlations that are weak due to low sample numbers.

4.3.5.1 Principal component regression

Principal component regression (PCR) was run in R using the pls package. PCR is a data transformation technique used to determine underlying relationships in complex datasets. PCR achieves this by reducing data dimensionality, forming new principal component (PCs), which are then used as predictors to fit a linear regression (stepwise) model. Each predictor was normalised, by dividing the predictor by its standard deviation. The PC were not rotated due to high correlation between variables. PC were calculated on the normalised total concentration of all elements above the detection limit, where elements were less than the detection limit concentrations could not be assigned therefore the method detection limit was used.

4.4 Results and Discussion

4.4.1 Glacial flour successfully enhanced crop yields

Himalayan and Iceland flour treatments were found to increase soybean yield (dry weight (g)) above control experiments (no treatment) by 85 % and 138 % respectively ($p < 0.05$) (Himalaya; 36.0 ± 2.9 g m^{-2}, Iceland; 47.4 ± 2.1 g m^{-2}, Control; 19.9 ± 3.4 g m^{-2}) (Fig 4.1A, Table 4.1) when applied to a low nutrient soil matrix at a practical application rate for farmers (2 T ha^{-1}) (Mohammed et al. 2014; Liu and Lal 2014). The resultant crop yield exceeded that via low-rate chemical fertiliser treatments ((N-P-K added at 10 kg ha^{-1} Figure 4.1A, Table 4.1). We also found that glacial flour application rate, over the range of 0.5 T ha^{-1} – 20 T ha^{-1}, was significantly positively correlated to soybean yield ($r^2 = 0.81$, $p < 0.05$) (Figure 4.1B).

The higher crop yield of the Icelandic flour (basalt) ($p < 0.05$) compared with the Himalayan flour (gneiss / granite) for the same application rate is likely explained by two inter-related factors. First, Icelandic flour had a higher total content of key plant essential nutrients (P, Fe, S, Mg, Ca, Mn), although it was depleted in K compared with the Himalayan flour, reflecting the local geology (Table 4.2). Second, the Icelandic flour was likely more susceptible to chemical weathering since the dissolution of basalt is faster than granite / gneiss (Goldich 1938). Basaltic rock is typically contains reactive minerals such as olivine, composed of isolated silica tetrahedra with intervening metal cations (e.g magnesium Mg^{2+}, iron Fe^{2+}), whereas gneiss-granite has a greater proportion of resistant minerals such as quartz (Goldich

1938). Furthermore, Icelandic flour had a smaller mean particle size, inferring a greater reactive surface area (mean p.s.d = 33.7 ± 1.7 µm), compared with Himalayan flour (mean p.s.d= 112.4 ± 2.3 µm) (Table 4.3). Concentrations of exchangeable nutrients (Ex-P; 24.6 ± 2.7 µg g^{-1}, Ex-K 1060 ± 94.6 µg g^{-1}, Ex-Fe 4.0 ± 0.08 mg g^{-1}) in Icelandic flour were also more than double those of the Himalayan flour (gneiss / granite) (Ex-P; 5.6 ± 0.8 µg g^{-1}, Ex-K 383 ± 67.7 µg g^{-1}, Ex-Fe 1.40 ± 0.02 mg g^{-1}) (Table 4.2).

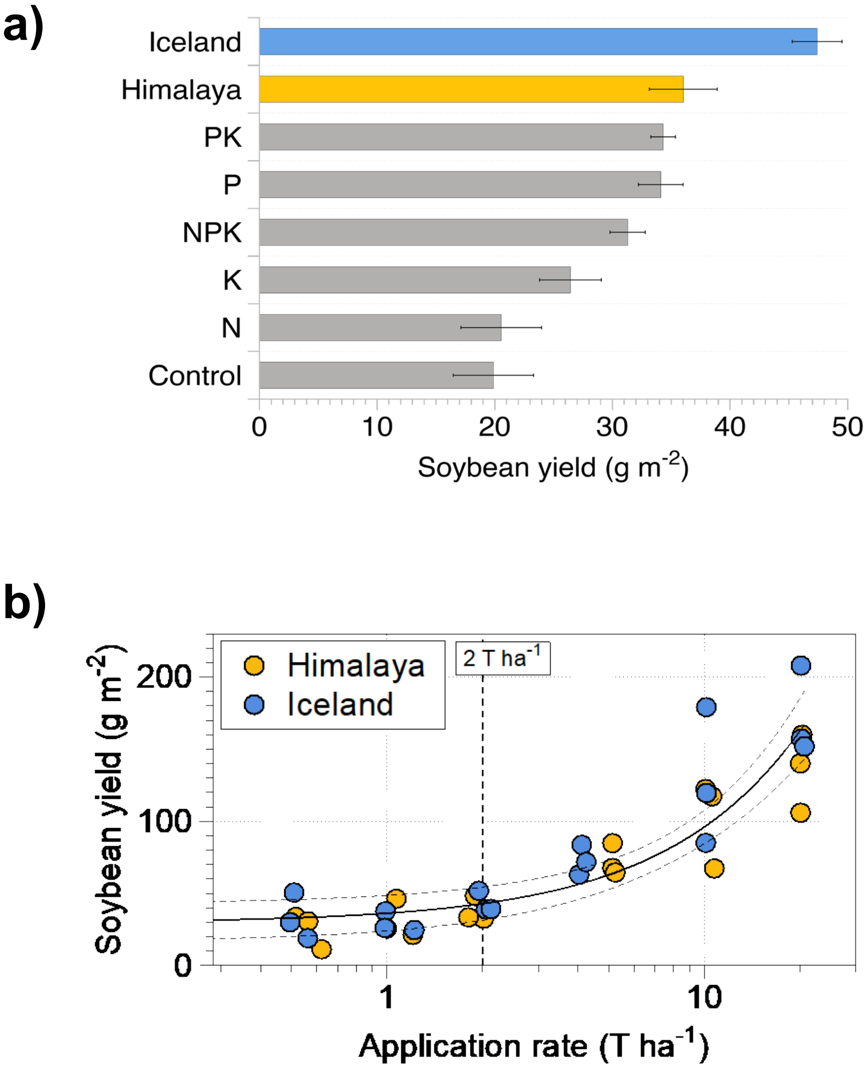

Figure 4.1 a) Soybean crop yield (g m^{-2}) across a range of treatments, including glacial flour applications at 2 T ha^{-1}, b) association between soybean yield and glacial flour application rate

Table 4.1: Soybean crop yield results (Glacial flour treatments shown are those for the 2 T ha^{-1} application rate). Treatments as follows - control is 'no additional treatment'. N = Nitrogen fertiliser, P = P fertsiliser, K = K fertiliser, PK = P + K fertiliser, NPK = N + P + K fertiliser, all at low rate.

Treatment	Soybean Yield		Change in FV/FM		Above ground biomass		Mean Nodules	n
	($g\ m^{-2}$)	(SE)	(%)	(SE)	(g per plant)	(SE)		
Control	19.9	± 3.4	- 31.1	± 1.5	1.24	± 0.17	28.3 ± 15.2	6
N	20.5	± 3.4	-23.4	± 2.7	1.56	± 0.08	31.1 ± 13.0	4
P	34.1	± 1.9	-20.5	± 1.8	1.95	± 0.06	86.9 ± 25.1	4
K	26.4	± 2.6	-24.6	± 1.2	1.84	± 0.10	79.6 ± 22.6	4
PK	34.3	± 1.0	*NA*	*NA*	1.71	± 0.26	91.3 ± 28.5	5
NPK	31.3	± 1.5	-24.6	± 1.9	1.91	± 0.12	51.8 ± 15.3	6
Himalaya flour	36.0	± 2.9	-17.6	± 2.1	1.92	± 0.02	105 ± 24	6
Iceland flour	47.4	± 2.1	-16.2	± 1.9	2.20	± 0.16	150 ± 38	6

Table 4.2: Measured mean glacial flour concentrations of plant essential exchangeable (uncrushed, labile extractions) and total nutrients (crushed, total extraction) Values from this study are presented to three significant figures.

	Exch-N	**Total-P (Exch-P)**	**Total-K (Exch-K)**	**Total-Fe (Exch-Fe)**	**Total-Ca**	**Total-Mg**	**Total-Mn**	**Total-S**	**Total-Si**	**Total-Zn**	**Total-Ni**	**Total-As**
Study site				*mg g^{-1}*							*ug g^{-1}*	
Sólheimajökull Glacier, Iceland ‘Icelandic flour’	< LOD	2.85 ± 0.04 (0.024 ± 0.003)	6.76 ± 0.15 (1.07 ± 0.09)	152 ± 2 (4.05 ± 0.08)	27.4 ± 0.46	33.5 ± 0.90	2.50 ± 0.70	3.56 ± 0.07	< LOD	232 ± 2.2	86.9 ± 2.9	2.59 ± 0.03
Chotta Shigri Glacier, Himalaya ‘Himalayan flour’	< LOD	2.24 ± 0.10 (0.006 ± 0.001)	8.41 ± 0.37 (0.38 ± 0.07)	20.5 ± 0.3 (1.49 ± 0.02)	2.35 ± 0.20	3.47 ± 0.89	< LOD	< LOD	1.02 ±0.17	114 ± 3.1	12.8 ± 0.2	73.8 ± 8.0

Table 4.3: Particle size data of Himalayan and Icelandic glacial flour. The equivalent diameter parameters are the diameters at 10 % (d[0.1]), 50 % (d[0.5]) and 90 % (d[0.9]) points on a particle size data curve. Data is presented to 3 significant figures or 1 decimal place.

Flour	**Mean**	**Equivalent diameter parameters**		
	(µm)	d [0.1] / µm	d [0.5] / µm	d [0.9] / µm
Himalaya	112.4 ± 2.34	19.6	88.3	234.5
Icelandic	33.7 ± 1.75	6.27	23.7	56.4

Both glacial-flours employed in this study clearly had a positive impact upon crop yield compared to recent field trials which applied Greenlandic freshwater glaciolacustrine-deposited glacial flour soils but showed no significant crop yield impact (Sukstorf 2020). This may be due to four related reasons (Sukstorf, Bennike, and Elberling 2020). First, the field trial used a mixture of timothy grass (*Phleum pratense*) and red fescue (*Festuca rubra*) that are not leguminous may be inherently less able to respond to glacial flour application in comparison with soybeans (*Glycine max*), a member of the legume family known to excrete organic acids to promote rock dissolution (Drever 1994; Oliveira Júnior, Prochnow, and Klepker 2011; Ta and Faris 1987). We also note that the Timothy grasses used in the Greenlandic study (Mojallali and Weed 1978) were not inoculated by rhizobium, as in our trials, which likely influenced their N-fixing capacity, crop productivity, and thus biological weathering. Second, we grew the soybeans at an average temperature of 19.5 °C, compared to 10.8 °C in the study using Greenlandic flour (Sukstorf, Bennike, and Elberling 2020). In addition, in contrast to the Greenlandic field study that suffered from water scarcity (Sukstorf, Bennike, and Elberling 2020), our soybean plants were well-watered throughout the experiment. The more favourable environmental conditions of our study, with warmer temperatures (19 °C) and 12 hr light / dark cycle is more applicable to the temperate low-latitude climate of mountain communities in the Himalayas during the agriculturally productive season (May – September) (Bhatt, Arunkumar, and Stanley 2015). Third, Greenlandic glacial flour derived from granitic bedrock may have a lower weathering capacity due to strong silicate quartz bonds in comparison to basaltic and gneiss rock (Hawkings et al. 2016). Finally, the Greenlandic glacial flour composed of Precambrian igneous metamorphic bedrock was determined to have a lower nutrient content than both Chhota Shigri Himalaya and Sólheimajökull Iceland flour as outlined in Chapter 3.

Agronomic Efficiency (AE) indices were computed (Table 4.4, Figure 4.2A, B), a widely used metric of the production impact of applied fertilisers to crop yield, to assess the efficacy of our glacial flour crop treatments compared with chemical fertilisers, allowing us to infer economic return (Equation 2; Methods) (Devasenapathy 2008). Since the flours include P and K traditionally assumed to be labile (i.e. associated with exchangeable species adsorbed to mineral surfaces) alongside less labile P and K associated with mineralogical phases (e.g. fluorapatite) AEs were calculated using both the exchangeable and total P and K (Tessier, Campbell, and Bisson 1979b).

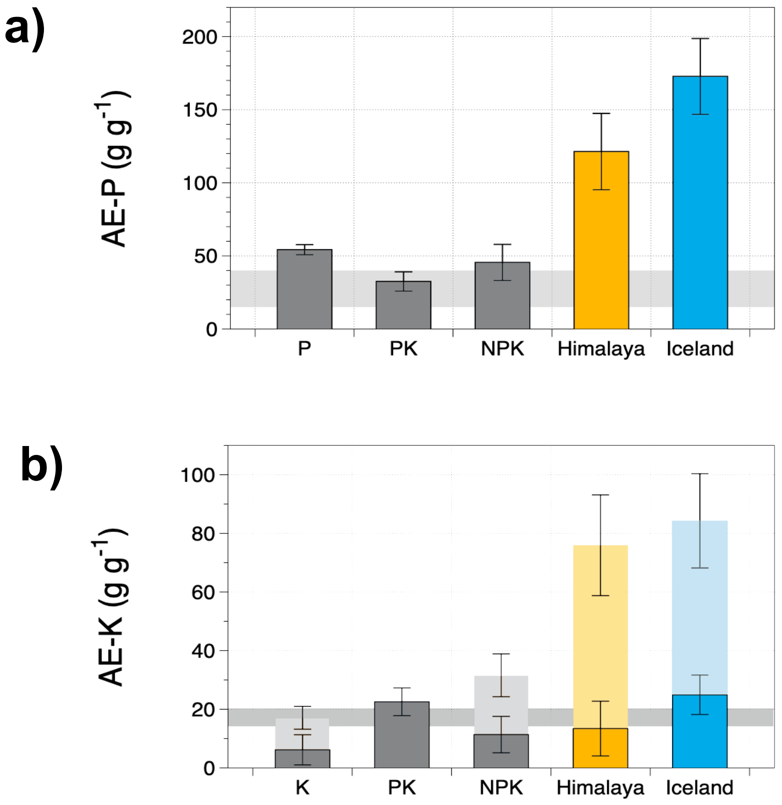

Figure 4.2: a) agronomic efficiency (AE-P) of P (g g^{-1}) **b)** agronomic efficiency (AE-K) of K (g g^{-1}). The grey shaded horizontal region in c) and d) are regarded as the optimum AE in farming (Chien, Prochnow, and Cantarella 2009). The darker coloured bars in c and d are AE calculated using the total K and P, and lighter colours are the AE calculated using the exchangeable AE-K values (these bars are not available for AE-P because the values calculated were beyond that of reasonable values, see main text). Agronomic efficiency calculations are calculated using the whole pot nutrient values of exchangeable or total nutrients, including the soil matrix.

Both glacial flours were more efficient per gram of exchangeable K than chemical K treatments (K 17.1 ± 3.9 g g^{-1}, PK 8.1 ± 1.6 g g^{-1}, NPK 31.5 ± 7.3 g g^{-1}, Himalaya 75.9 ± 17.2 g g^{-1}, Iceland 84.3 ± 16.1 g g^{-1}). However, the same analysis for exchangeable P also revealed very high implausible AE values (Himalaya flour 3100 ± 212 g g^{-1}, Icelandic flour 4609 ± 240 g g^{-1}), that are two orders of magnitude higher than International Fertiliser Association (IFA) recommended values AE values (15 – 40 g g^{-1}) (Roy et al. 2006; Fixen et al. 2015). AEs calculated using total-P from glacial flour extractions were similar to recommended AE-P values, indicating that the mineral P associated with the flours (likely fluorapatite; extractable using a HCl solution) could be utilised by plants after it is released by biogeochemical weathering during the experiments (Cross and Schlesinger 1995; Hawkings et al. 2016). The sequential P extractions show that the majority (> 95 %) of Total-P in the uncrushed glacial flours is held in the HCl bound phase (Table 4.5). This is an interesting finding since it suggests that mineral P in rocks, traditionally assumed to be of low bioavailability, can be accessed during crop growth due to enhanced weathering.

Table 4.4: Agronomic Efficiency. Agronomic efficiency of P (AE-P) and K (AE-K). Relevant efficiency data is presented. AE-P was calculated based on Total P concentrations. AE-K was calculated from Total K, AE-Exch-K is presented based on sequential K extractions. FAO recommended soluble fertiliser application rate also included for comparison. Values from this study are presented to three significant figures.

Treatment	AE-P	AE-K *(g g^{-1})*	AE-Ex-K	n
P	54.3 ± 3.46	-	-	12
K	-	6.15 ± 5.15	17.1 ± 6.15	12
PK	32.5 ± 6.59	22.5 ± 4.73	8.11 ± 0.56	12
NPK	45.5 ± 12.3	11.4 ± 6.21	31.6 ± 7.28	12
Himalaya (2 T ha^{-1})	121 ± 26.1	13.4 ± 9.34	75.9 ± 17.2	12
Iceland (2 T ha^{-1})	173 ± 25.9	24.9 ± 6.72	84.3 ± 16.1	12

Table 4.5: Phosphorus extraction data for Himalayan and Icelandic glacial flours on uncrushed, dry glacial flour. Data is presented to 3 significant figures or 1 decimal place. HCl-P forms 99 % and 97 % of P in uncrushed Himalayan and Icelandic flour respectively. Exchangeable P (MgCl-P + NaOH-P) is 0.8 % and 2.5 % of Himalayan and Icelandic flour in uncrushed rock.

	MgCl-P	NaOH-P	HCl-P	Res-P / POP	Total P (uncrushed)	Total P (crushed)	n
Flour	*(µg g^{-1} (Dry sediment))*						
Himalaya	1.2 ± 0.5	4.4 ± 2.7	724 ± 52	3.1 ± 2.6	733 ± 61	[2240 ± 10]	9 [3]
Iceland	9.8 ± 0.6	14.8 ± 5.4	1235 ± 80	5.2 ± 2.1	983 ± 95	[2850 ± 40]	9 [3]

Minimum estimates of AE, using total P and K in calculations, indicated that glacial flour applied at 2 T ha^{-1} was more efficient in improving crop yields than low rate (10 kg ha^{-1}) chemical fertilisers (Figure 4.2A and B, Table 4.4). All AE-P indexes exceeded the optimum range for agriculture (15 – 40 g g^{-1}) (Roy et al. 2006; Fixen et al. 2015). However, only PK and Icelandic flour treatments met the optimum range for AE-K (16 - 20 g g^{-1}) (Figure 1D, Table 3) (Roy et al. 2006; Fixen et al. 2015). The reduced efficiency of chemical fertilised treatments compared to glacial flour suggest that a proportion of the chemical nutrients may have become unavailable following application. Reduced nutrient availability could be due to microbial competition and uptake, or rapid sorption to the artificial soil matrix (Sager, Park, and Chon 2007). Overall, our calculated AE-P and AE-K for glacial flours were within the acceptable ranges published for agriculture (Figure 4.2A,B) (Fixen et al. 2015). We note that they are also likely to be minimum estimates since a strong acid (HCl + HNO_3) extraction method used to determine the total nutrient content of glacial flour giving an inflated estimate of the total P and K present in the artificial soil. Overall, our results suggest that the weathering of primary rock minerals in glacial flour-treated soils have the potential to act as a significant source of bioavailable P and K.

4.4.2 Glacial flour improved N fixing capability and reduced stress

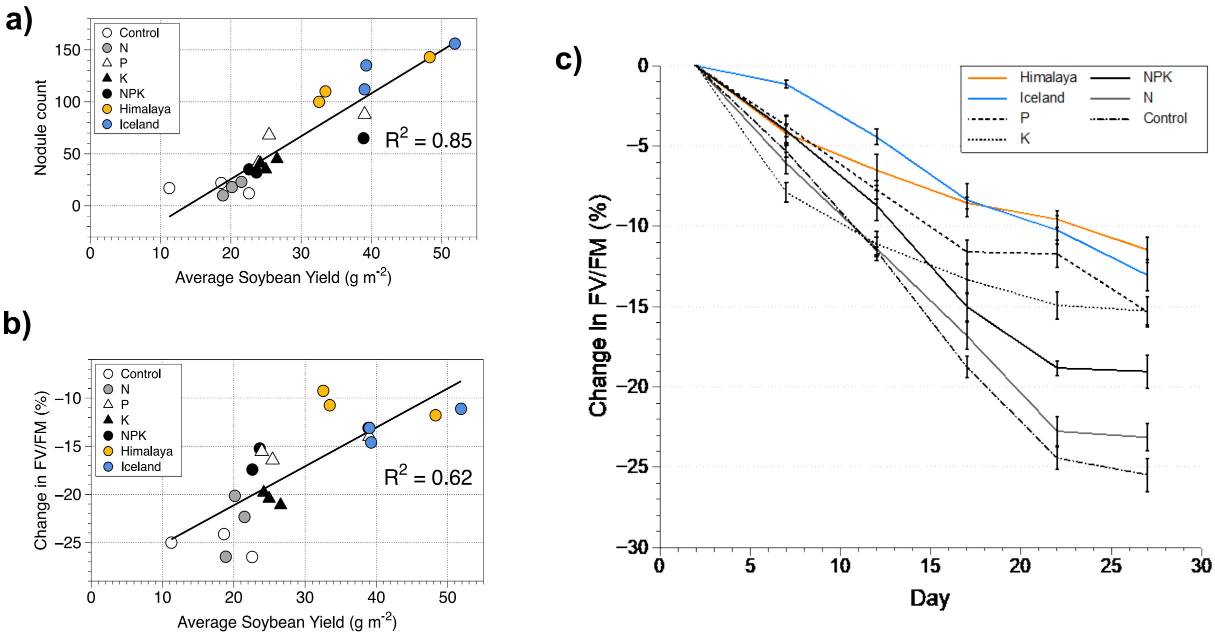

Figure 4.3 a) Linear regression of nodule count and average soybean yield across all experiments, $R^2 = 0.85$, b) Linear regression of the percentage change in FV/FM compared to Day 0 and average soybean yield (g m^{-2}), c) Time series of FV/FM (%) over the first month of the experiment for all treatments (27 days).

To assess the effect of glacial flour application on biological nitrogen fixation (BNF) and the levels of stress in the soy bean plants, we performed root nodule counts and measured photosynthetic capacity (FV/FM; ratio between variable fluorescence and maximum fluorescence, representing the maximum potential quantum efficiency of Photosystem II if all capable reaction centres were open) (Murchie and Lawson 2013; Maxwell and Johnson 2000). Both parameters correlated positively with crop yield in all experimental treatments ($p < 0.05$, $r^2 = 0.85$ and $p < 0.05$, $r^2 = 0.62$, respectively) (Figure 4.3A, 2B, Table 1). Over the first 30-days all plants exhibited reductions in FV/FM across all treatments (Figure 4.3C), suggesting that they were experiencing rising stress. However, the plants receiving the glacial flour treatments (2 T ha^{-1}) displayed the lowest reduction in FV/FM by the end of the experimental period. Final FV/FM ratios for Himalayan flour (0.655 ± 0.003) and Icelandic flour (0.662 ± 0.004), showed a 16.2 ± 0.5 % and 17.6 ± 0.8 % reduction in FV/FM ($p < 0.05$) during the experiment, compared to a 31.1 ± 1.5 % reduction in the control treatment and in chemical fertiliser treatments, N -23.4 ± 2.7 %, P -20.5 ± 1.8 %, K -24.6 ± 1.2 %, and NPK -24.6 ± 1.9 % (Table 4.1, Table 4.6 for original dataset). The glacial flour-treated soybeans also had the highest mean nodule counts (Himalaya 105 ± 11 average nodules per plant, Iceland 150 ± 19 average nodules per plant).

The success of glacial flour at enhancing BNF capacity and supporting plant growth, compared to chemical fertilisers, is likely due to three reasons. First, the low-N soil matrix and glacial flour treatments may have up-regulated nodule development, whereas chemical N treated pots likely had nodule development down-regulated, which is commonly observed in chemical N fertilised crop land (Ferguson et al. 2010). Second, it is likely that soybeans with lower nodule counts remobilised N from their leaves to the grain, diminishing their photosynthetic capacity as indicated by a steep reduction in FV/FM, and subsequently limiting crop yield (Mengel 1994). This is likely because at the start of the experiment, chemical N-treated pots were likely to have taken up the N rapidly into crop biomass, but then further N supplies were unavailable for growth. Third, prolific nodule growth is dependent on the availability of P and micronutrients (Fe, S, Mo and V), potentially supplied by glacial flour but not by chemical fertilisers (Smith 1992b), which is a hypothesis explored in more detail below.

Our data suggest that glacial flours acted as a source of both macro and micronutrients in our controlled growth experiments. To explore potential links between the supply of essential plant nutrients (P, K, Fe, Mg, Ca, Si, Mn, Zn, Ni and S) and soybean crop yield, we performed a Principal Components Regression (PCR). We combined a Principal Component Analysis (PCA) upon essential plant nutrients (P, K, Fe, Mg, Ca, Si, Mn, Zn, Ni and S) in treatment pots, followed by a stepwise regression analysis, which employed soybean yield as the dependent variable and the scoring coefficients of principle components (PCs) at each sampling location as independent variables. The first two components of our PCA accounted for > 99 % of the total variability in pot nutrient content, PC1 77.1 % and PC2 22.0 % (Figure 4.4). In PC1, Icelandic flour was responsible for 79.8 % of variation, whilst Himalayan flour only accounted for 13.8 %. This pattern is reversed for PC2, with a contribution of 82.4 % for Himalaya flour, compared to 16.3 % for Icelandic flour. Elemental loadings on PCs reinforce the likely importance of additional micronutrients in plant growth. PC1 had high loadings for Zn (0.99), Ni (0.97), Ca (0.95), P (0.93), S (0.92), Mn (0.92) and Mg (0.90) (all high in Icelandic flour), whilst PC2 had a higher loading for Si (0.97), likely reflecting the high concentration in Himalayan flour (Total Si 1.02 ± 0.17 mg g^{-1}) (Table 2). Furthermore, although K and Fe had relatively high loadings in PC1 (0.81 and 0.89), they were the only nutrients with similar loadings in PC2 (0.58 and 0.45). Using the PC scores as factors within a PCR, we determine that 79.2 % of the variance in soybean crop yield can be explained by PC1 and 24.7 % of the variance by PC2 (Total PC1 + PC2 = 99.9 %, $p < 0.0001$, $r^2 = 0.91$), suggesting that glacial flour supplies both essential macro and micronutrients that can support crop and plant health. While prior research into crushed rock for agriculture has focused on the enhancement of P and K in crop growth experiments, our results suggest that glacial flour improves soil fertility via increasing soil macro- and micro-nutrient content.

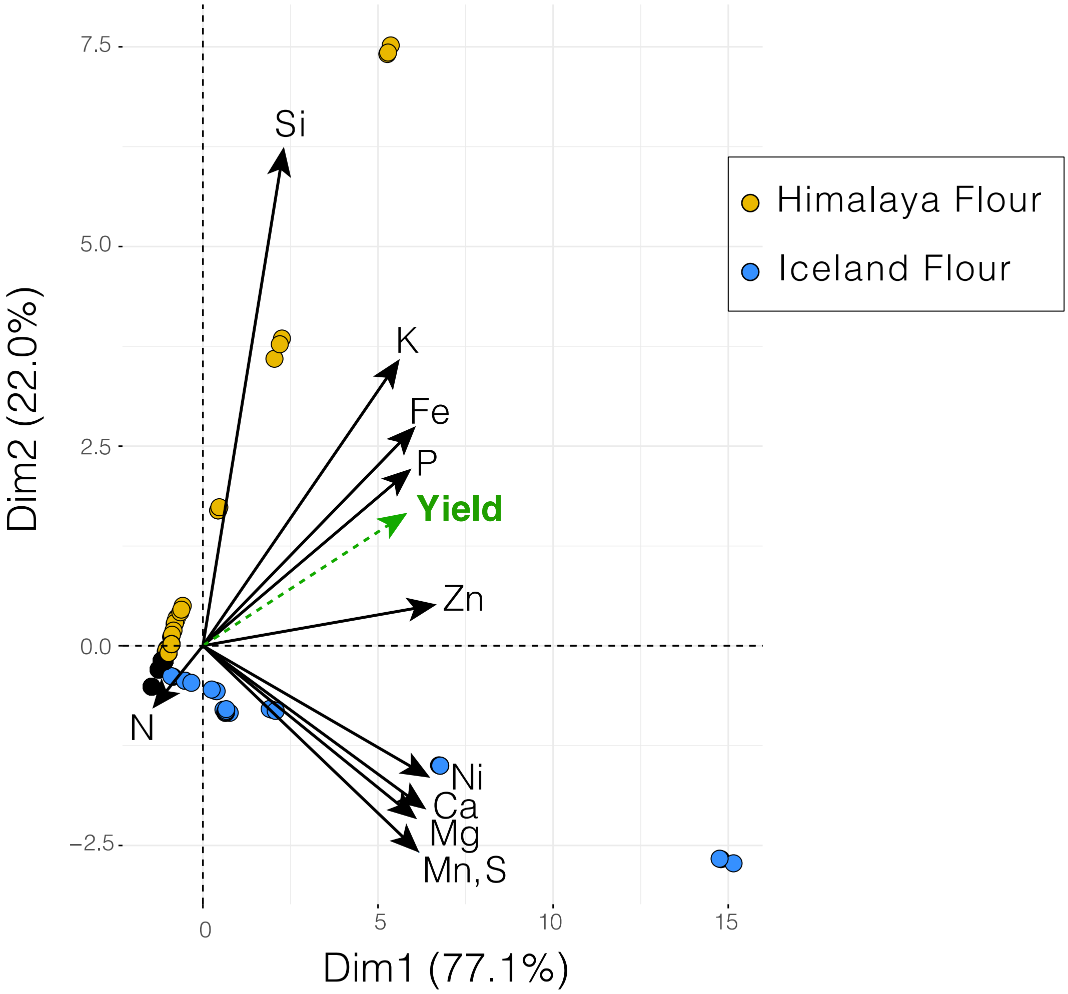

Figure 4.4: PCA of glacial flour pot nutrients and crop yield. Indicating importance of Dimension 1 (77.1 %) and Dimension 2 (22.0 %).

Table 4.6: FV/FM Scores across the 60-day experiment, shown to 3 significant figures.

Day	**Treatment**						
	Control	**NPK**	**P**	**K**	**N**	**Himalaya**	**Iceland**
2	0.805 ± 0.018	0.812 ± 0.017	0.803 ± 0.016	0.793 ± 0.015	0.791 ± 0.017	0.794 ± 0.015	0.790 ± 0.015
7	0.762 ± 0.036	0.748 ± 0.043	0.773 ± 0.016	0.761 ± 0.035	0.743 ± 0.018	0.773 ± 0.015	0.781 ± 0.016
12	0.712 ± 0.023	0.722 ± 0.018	0.741 ± 0.072	0.724 ± 0.028	0.701 ± 0.065	0.730 ± 0.018	0.755 ± 0.019
17	0.654 ± 0.019	0.704 ± 0.025	0.71 ± 0.084	0.674 ± 0.025	0.658 ± 0.026	0.710 ± 0.011	0.724 ± 0.022
22	0.610 ± 0.022	0.691 ± 0.021	0.709 ± 0.035	0.620 ± 0.018	0.611 ± 0.056	0.698 ± 0.025	0.709 ± 0.018
27	0.600 ± 0.023	0.688 ± 0.016	0.680 ± 0.018	0.610 ± 0.025	0.608 ± 0.045	0.688 ± 0.029	0.687 ± 0.029
32	0.600 ± 0.022	0.655 ± 0.044	0.682 ± 0.021	0.605 ± 0.023	0.600 ± 0.053	0.677 ± 0.015	0.680 ± 0.015
37	0.600 ± 0.025	0.640 ± 0.031	0.665 ± 0.017	0.600 ± 0.024	0.601 ± 0.018	0.670 ± 0.023	0.678 ± 0.023
45	0.600 ± 0.029	0.635 ± 0.034	0.650 ± 0.022	0.605 ± 0.042	0.595 ± 0.029	0.650 ± 0.026	0.669 ± 0.026
55	0.600 ± 0.035	0.630 ± 0.031	0.644 ± 0.038	0.600 ± 0.032	0.600 ± 0.021	0.655 ± 0.018	0.666 ± 0.018
60	0.555 ± 0.014	0.622 ± 0.020	0.638 ± 0.020	0.598 ± 0.012	0.595 ± 0.028	0.654 ± 0.022	0.662 ± 0.022

4.4.3 Glacial flour: toxin or treat?

Enhancing the nutritional value of soybeans by boosting micronutrient concentrations ('biofortification') may be of significant global benefit in addressing micronutrient malnutrition (e.g. Zn) (White and Broadley 2009; Cakmak 2008) which particularly impacts some low income rural communities in Low and Middle-Income Countries (Asia 2018). Conversely, some trace elements may be detrimental to human health when found at high concentrations, with previous research expressing concern related to potential mobilization of toxic metals (e.g., Cr, Ni, As, Pb) from crushed rock within the soil matrix (Beerling et al. 2018b). Here, we focus on two beneficial trace elements sourced from rock weathering within the soil, Zn and selenium (Se), which play essential roles in human health (Roohani et al. 2013; Hambidge 2000). We also evaluated concentrations of Cr, Ni, Pb and arsenic (As) in the soybean crop, since these have been shown to cause adverse human health impacts in Asia (Fordyce 2013; Andersen 2002; Kaur, Mehra, and Kumar 2022). Potential bioaccumulation of trace elements in our soybean experiments was calculated using enrichment factors, where the concentration of nutrient (e.g. Zn mg g^{-1}) in the sample was divided by the concentration in the control experiment (mg g^{-1}) to give the bean enrichment factor (EF mg mg^{-1}) (Kisku, Barman, and Bhargava 2000).

We show that both glacial flours have the potential to drive bioaccumulation of trace elements in soybean crops. Beneficial trace elements, Zn and Se, displayed an EF above the chemical fertiliser NPK treatment (Figure 4.5A, B, Table 4.7, $p < 0.05$). NPK treated soybeans were depleted in all trace elements compared to the control and glacial flour treatments, likely due to limited trace elements in the artificial soil matrix which when growing a higher crop yield due to the provision of NPK, were unable to meet the soybean trace element needs. Soybeans had mild Zn enrichment (EF < 1.5 mg mg^{-1}), which occurred in all flour treatments and was independent of both the glacial flour application rate and the total Zn concentration in the flour (Icelandic flour 232 ± 2.2 μg g^{-1}, Himalayan flour 114 ± 3.1 μg g^{-1}) (Figure 4.5A Table 4.7). There was significant enrichment of Se in Icelandic flour treated beans, Icelandic flour achieved high levels of enrichment (>2 mg mg^{-1}) across all doses and was dose dependent. However, no significant enrichment was observed for Himalayan flour although individual soybeans were enriched (Figure 4.5B). This may be due to the lower Se concentrations in Himalayan flour compared to Icelandic flour (3.5 ± 0.5 μg g^{-1} compared to 6.0 ± 0.2 μg g^{-1}) and lower rock dissolution rates, resulting in a slower and reduced availability of Se.

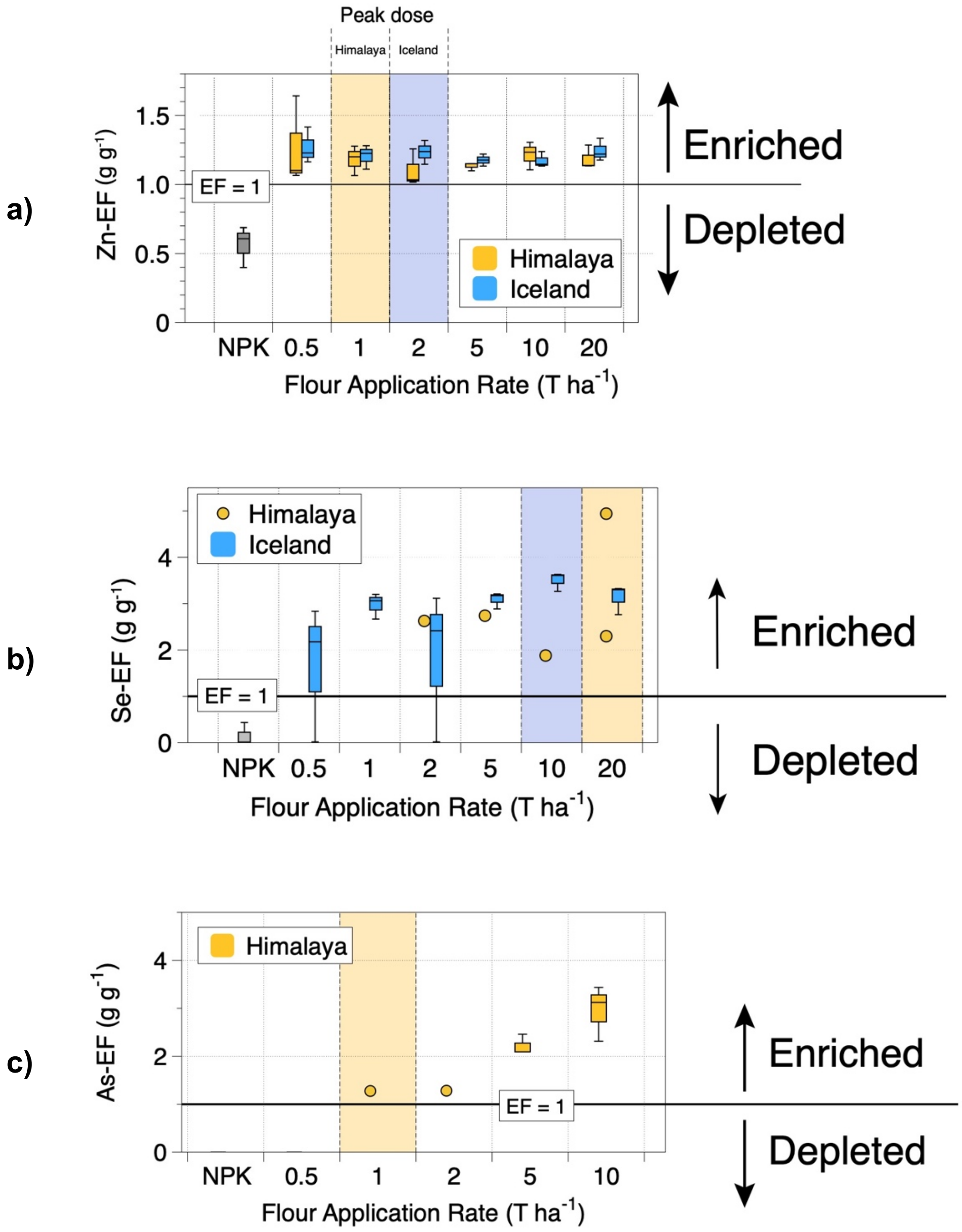

Figure 4.5 Enrichment actors for: a) Zn (Zn-EF g g^{-1}); b) Se (Se-EF g g^{-1}); and c) As (As-EF g g^{-1}) for glacial-flour (0.5 – 20 T ha^{-}1) and NPK amended experiments. The shaded regions are the dose with the highest EF, Yellow for Himalaya and Purple for Iceland. An EF of 1 is plotted, where points above and below the line are enriched and depleted respectively in the element in question. Data points for Se-EF in Himalayan glacial flour treatments are plotted as single points since undetectable levels were recorded in some pot replicates. As-EF reports only Himalayan data since As in both NPK and Icelandic treatments were below detection.

Table 4.7: Soybean concentrations of chosen metals, uptake, and enrichment factors (EF). Values from this study are presented to three significant figures. Values in brackets are single replicate results only. Where the control treatment was below the LOD for Total As, the method detection limit was used, shown in italics, for enrichment factor calculations only.

		Zinc			Selenium			Arsenic			
Treatment		Bean Zn Concentration *(μg g^{-1})*	Zn Uptake *(μg)*	Zn-EF *(g g^{-1})*	Bean Se Concentration *(μg g^{-1})*	Se Uptake *(μg)*	Se-EF *(g g^{-1})*	Bean As Concentration *(μg g^{-1})*	As Uptake *(μg)*	As-EF *(g g^{-1})*	n
Control		73.2 ± 5.2	23.8 ± 5.8	-	42.1 ± 8.5	13.1 ± 2.3	-	*0.8 (LOD)*	-	-	3
NPK		41.2 ± 8.9	42.4 ± 15.9	0.56 ± 0.12	51.4 ± 26.7	33.5 ± 7.2	0.22 ± 0.21	-	-	-	3
Himalaya	0.5 T ha^{-1}	95.6 ± 7.7	59.5 ± 6.9	1.31 ± 0.11	-	-	-	-	-	-	3
	1.0	105 ± 12.0	88.0 ± 12.6	1.43 ± 0.17	-	-	-	(1.02)	(0.73)	(1.28)	3
	2.0	92.7 ± 19.2	92.4 ± 20.4	1.27 ± 0.26	(110)	(107)	(2.63)	(1.03)	(1.02)	(1.28)	3
	5.0	86.2 ± 6.4	112 ± 9.1	1.18 ± 0.09	(115)	(144)	(2.74)	1.77 ± 0.14	2.29 ± 0.22	2.21 ± 0.17	3
	10.0	80.5 ± 8.0	124 ± 8.7	1.10 ± 0.11	(79.0)	(132)	(1.88)	2.37 ± 0.38	3.67 ± 0.61	2.96 ± 0.47	3
	20.0	82.7 ± 1.8	135 ± 15.0	1.13 ± 0.02	(96.5 – 208)	(137 – 350)	(2.29 – 4.94)	3.28 ± 0.29	5.34 ± 0.56	4.10 ± 0.36	3
Iceland	0.5 T ha^{-1}	88.7 ± 6.0	66.4 ± 10.7	1.21 ± 0.08	105 ± 13.9	49.5 ± 6.3	2.51 ± 0.33	-	-	-	3
	1.0	86.6 ± 5.1	78.0 ± 8.4	1.18 ± 0.07	125 ± 9.5	113 ± 12.2	2.97 ± 0.32	-	-	-	3
	2.0	92.7 ± 7.8	101 ± 20.1	1.27 ± 0.11	116 ± 14.7	77.3 ± 5.6	2.77 ± 0.35	-	-	-	3
	5.0	87.9 ± 5.2	113 ± 5.2	1.21 ± 0.07	130 ± 6.1	167 ± 10.5	3.09 ± 0.14	-	-	-	3
	10.0	90.1 ± 5.1	146 ± 11.6	1.23 ± 0.07	147 ± 7.0	237 ± 15.2	3.50 ± 0.17	-	-	-	3
	20.0	85.9 ± 2.6	168 ± 3.1	1.18 ± 0.04	133 ± 10.9	257 ± 20.0	3.13 ± 0.26	-	-	-	3

Recommended daily allowances (RDA), indicate that Zn requirements are between 6.5 and 9.4 mg day^{-1}, and dietary Se is classed as deficient at < 40 µg day^{-1} and toxic at > 400 µg day^{-1} (World Health Organization 2004b). The theoretical dietary supply of Zn and Se for a portion of raw soybeans (35 g) grown in our experiments was calculated using the total element concentration of the soybeans. A portion of soybeans grown in Himalayan flour applied at a low dose of 1 T ha^{-1} (yellow shaded area, Figure 4.5A) provides 33.0 ± 2.4 % of the recommended daily dietary Zn (3.19 ± 0.37 mg of total Zn) and no significant Se intake However, Icelandic flour applied at the same dose (1 T ha^{-1}) would supply 35.4 ± 2.9 % of daily dietary Zn and 952 ± 72.7 % of the recommended intake of Se. Although by current measures soybeans grown with Icelandic flour might be regarded as Se-toxic, consumption of the beans grown in 1 T ha^{-1} Icelandic flour treated pots would result in an intake of 1940 ± 450 µg of Se, above the daily recommended intake limit of 400 µg (FAO / World Health Organization 2011) There is considerable uncertainty surrounding recommended dietary Se consumption. Moderately high Se diets (> 0.1 mg) have been shown to be anticarcinogenic, highlighting additional work is needed to clarify safe dietary Se intake (Li et al. 2004). It is also important to ascertain whether these Se enrichment levels are achieved in real-world conditions. For example, the bioavailability of Se has been shown to be higher in calcareous soils (pH 7.87) than yellow brown soils (pH 5.68) (Deng et al. 2021). Nevertheless, low doses of glacial flour appear to biofortify crops in beneficial elements indicating that their further investigation could yield promising results via field trials.

Glacial flour treated soybeans all displayed undetectable levels of toxic heavy metals Cr, Ni and Pb (Limit of detection (LODs): Cr 2.75 µg g^{-1}, Ni 6.28 µg g^{-1}, Pb 2.79 µg g^{-1}). As was also undetectable in all Icelandic flour treated soybeans (LOD < 0.8 ug g^{-1}). However, there was significant As enrichment in Himalayan flour-treated beans with clear dose dependency for application rates above 0.5 T ha^{-1} (Figure 4.5C, Table 4.7, $p < 0.05$). The As in Himalayan flour was likely sourced from bands of meta-sedimentary rocks rich in pyrite beneath Chhota Shigri glacier (Kumar, Kumar Singh, et al. 2020). Toxic levels of As in humans resulting in chronic impacts to health (arsenicism) are believed to occur at doses of > 100 µg day^{-1} (Organization 2022), however, this is likely to be a conservative estimate because it is estimated from drinking water concentrations where As is highly bioavailable (Organization 2017). Soybeans grown in Himalayan flour at a dose required to achieve Zn biofortification (0.5 T ha^{-1}) did not have a measurable Total As concentration. However, a portion (75g) of soybeans grown in Himalayan flour at a high dose rate (5 T ha^{-1}) would result in an As intake of 44.2 ± 1.8 µg, although this is below the daily limit for arsenicism, the cumulative impact of consuming all an individual's dietary needs from crops enriched in As is likely to exceed toxic limits. Although total As levels alone do not indicate full toxicity to humans, As speciation (e.g. organo As species, As^{3+} and As^{5+}) plays a critical role in potential toxicity and should be investigated in the farm to fork cycle (Koch et al. 2000).

The enrichment of As in glacier flour-amended soybeans also highlights the potential of Himalayan glacial flour as a source of As contamination to communities (Kumar, Kumar Singh, et al. 2020; van Geen et al. 2019). For smallholder subsistence farmers with a diet mostly sourced from crops grown on their land this low level of arsenicism may be of concern. Although it is unlikely glacial flour amendments would be sourced directly from the glacier terminus, these findings indicate a need to better understand the potential toxicity of soils within deglaciated landscapes and on glacial sediment floodplains, for example in the Punjab floodplain and the high Himalaya (Kumar, Kumar Singh, et al. 2020). Improving the temporal and spatial understanding of glacial flour micronutrient and trace element supply is critical to inform future work.

4.4.4 The future of glacial flour in agriculture

We have shown that glacial flour enhances crop yields and improves plant health and nutrient and micro-nutrient content, summarised in Figure 4.6. Glacial flour appears to act as a source of P, K and micronutrients to soybeans, with optimum holistic benefits when applied at 2 T ha^{-1}, with higher yields achievable with increased flour dosage. These results are consistent with previous research on crushed rock application to soils, where positive effects upon crop yield occurred at a minimum of 2 T ha^{-1} but with significant yield gains at higher doses (Mohammed et al. 2014). Current enhanced weathering research typically applies a minimum of 10 T ha^{-1} of crushed rock as a CO_2 sequestration strategy and crop yield enhancement (Beerling et al. 2020; Beerling et al. 2018b). However, high application rates of crushed rock across large areas of croplands have sustainability issues and have failed to assess wider biogeochemical implications (e.g., toxicity). We note that the optimum application of glacial flour to improve crop yield, nutrition and plant health might be best achieved at a small-scale within subsistence zero-budget farming networks (e.g., composting, bokashi). For example, applying a small amount of glacial flour (<2 T ha^{-1}) to an organic fertiliser (e.g., manure) may boost crop growth and nutrition (Zn, Se intake).

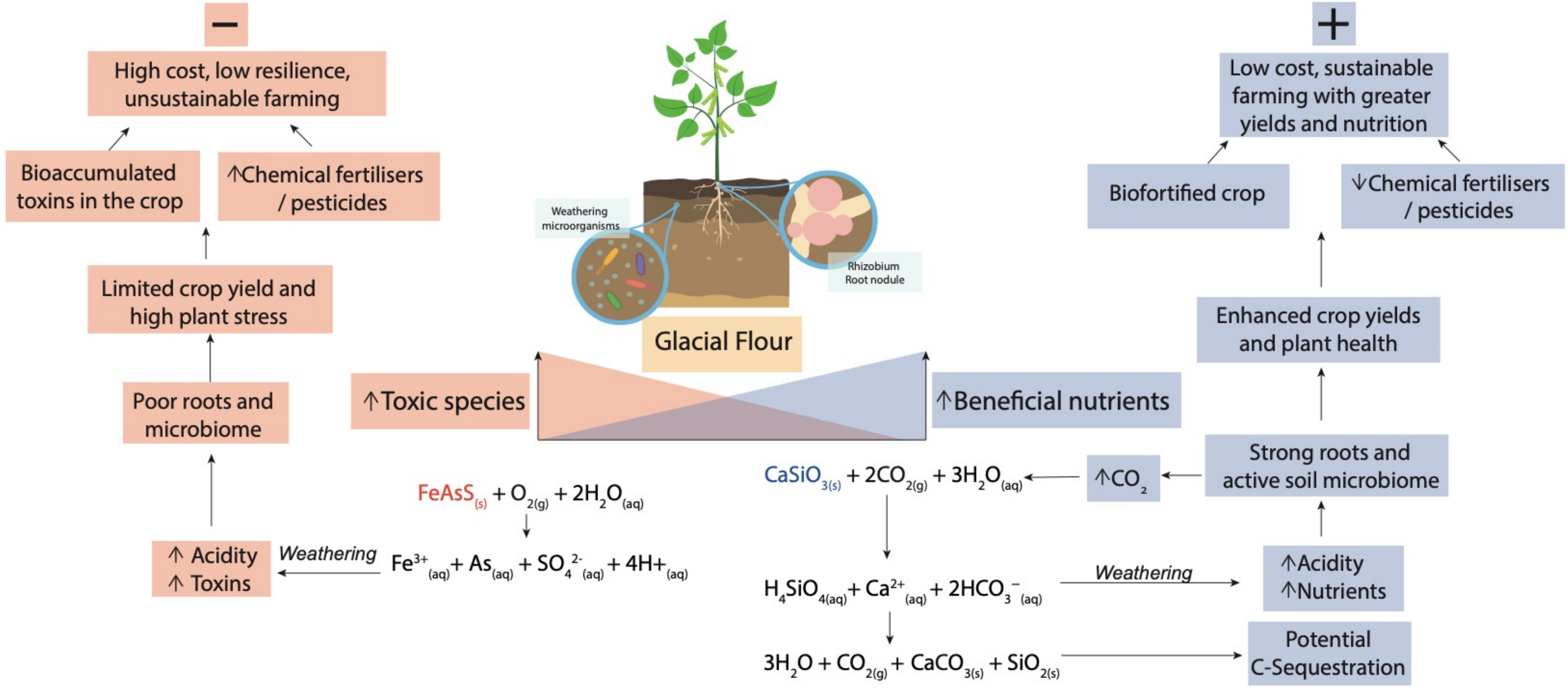

Figure 4.6: Conceptual diagram of glacial flour as a soil amendment or potential source of toxic elements. As glacial flour weathers two biogeochemical pathways are possible – (i) either glacial flour releases nutrients into the soil that stimulates a cascade of positive impacts upon the soil health and then crop growth and yield, and/or (ii) glacial flour releases toxic elements that negatively impact soil, crop yields and human health. Hypothetically, the enhanced crop health and yield results in a reduction of intensive farming strategies, shifting towards more sustainable agricultural methods. However, glacial flours that are high in toxic elements may result in farmers looking to amend soils with conventional practices. Greater use of chemical fertilisers and enhanced bioaccumulation of potentially toxic elements (e.g., As, Se), results in high cost – low resilience unsustainable farming.

For such small-scale application, glacial flour could be acquired locally from areas where the build-up of sediment causes mechanical, logistical and/or maintenance issues (e.g., hydroelectric dams, reservoirs, and harbours), potentially stimulating circular economies. The focus in the literature thus far has been on the fertilisation potential of glacial flour exported from large ice sheets such as the Greenland Ice Sheet and the Antarctic Ice Sheet into the marine environment, but with far less consideration of impacts on terrestrial landscapes downstream of significant glacier sources, such as Himalaya, Andes, Arctic glaciers (Hawkings et al. 2016; Hawkings, Skidmore, Wadham, Priscu, Morton, Hatton, Gardner, Kohler, Stibal, and Bagshaw 2020; Hawkings et al. 2017; Hawkings et al. 2015a; Hawkings et al. 2014; Raiswell et al. 2018; Wadham et al. 2016). Our results also caution that some glacial flours may also act as a source of toxic elements to crops and downstream ecosystems (e.g., As). Thus, scrutiny of the underlying bedrock geology and a better understanding of elemental speciation must form part of any future strategies for glacial flour soil application to soils, or agricultural expansion in mountainous terrain.

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Chapter 5.

Toxin or treat? Glacial flour as a source of beneficial micronutrients and toxic trace elements in crops

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S.T., J.L.W., J.T., and J.R.H conceived the project. S.T., J.L.W., J.T., J.R.H., G.L.-G., A.L.R., performed the fieldwork, collected samples, and provided logistical support. S.T. and J.L.W designed and conducted the crop growth investigation. S.T., S.F., C.A.Y., F.S undertook geochemical analysis. J.L.W funded the research. A.H provided plant research facilities. S.T. analysed the data and wrote the manuscript with input from J.L.W., J.T., S.F., J.R.H and contributions from all other co-authors.

5.1 Abstract

Mountain communities face multiple future challenges associated with meeting future food demands whilst increasing sustainability against the backdrop of increasing impacts of climate change. Prior research has determined that glacial flour, the finely crushed rock created through communition between ice and bedrock, has potential as a novel sustainable strategy to increase crop yields and improve plant health. The potential for glacial flour to drive bioaccumulation of trace elements which might either serve as essential nutrients and/or toxins for human consumption (As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Pb, S, Se, Sr, Zn) has been largely unexplored but is important to consider if glacial flour were to be used to enhance crop yields in the future by improving soil nutrient status. Alongside the potential use of glacial flour as a soil enhancer, future agriculture is likely to expand into deglaciating regions facing recent glacial retreat such as high latitude and high altitude, populated areas (e.g., Himalayas), making consideration of the potential for bio-accumulation of trace elements in the arising crop critical to consider. This thesis will evaluate the potential for glacial flour- treated soils to cause bioaccumulation of trace elements in leguminous crops (soybean *Glycine max.* var Black jet) via a glass house investigation. This thesis chapter indicates that glacial flour from two glaciers, Chotta Shigri, Indian Himalaya and Sólheimajökull glacier, Iceland has the potential to enhance both beneficial and potentially toxic elements. Notably, Himalaya and Iceland glacial flours applied at a rate of 2 T ha^{-1} increased beneficial soybean total-Zn to achieve 116 ± 14 % and 120 ± 14 % of the recommended dietary Zn intake. However, Himalaya glacial flour treated crops also had toxicity issues, with significant As bioaccumulation across the 0.5 – 20 T ha-1 investigated application rates, 20 T ha^{-1} increased dietary As consumption 2.5 times the WHO safe daily limit (246 ± 3 ug compared to 100 ug).

5.2 Introduction

The concentrations of trace elements in crops (As, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, P, Pb, S, Se, Sr, Zn) (TE) are determined by the soil, crop type and farming soil fertilisation strategies, and can result in 'bioaccumulation', where the concentration of the TM in the crop is significantly higher than in the soil. TE concentrations can have associated beneficial or harmful impacts on the quality of the crop for human consumption. The bioaccumulation of beneficial elements is seen as a potential strategy to enhance food crop nutrition content, termed ‘biofortification’. ‘Biofortification’ is a deliberate strategy in which the nutritional value of crops can be enhanced via either transgenic crops, breeding or agronomic practices, such as micronutrient soil treatments (Saltzman et al. 2013). This becomes pertinent given that micronutrient malnutrition afflicts over 2 billion worldwide, predominantly women, infants and children from resource poor areas in the Global South (Micha et al. 2020).

For normal function, human bodies require 14 micronutrient minerals; Mg, S and Cl (< 100 mg per day) and B, Fe, Mn, Cu, Zn, Ni, Mo, Na, Se, Co and I (< 10 mg per day) (Organization 2004a). Micronutrient deficient diets can cause significant health problems, from severe and life-threatening conditions (e.g. blindness, goitre, immune dysfunction and anaemia) to limiting cognitive function and ability, thus reducing potential human productivity and working capacity, termed ‘hidden hunger’ (Bhaskaram 2002; Ramakrishnan 2002b; Kennedy, Nantel, and Shetty 2003; Gödecke, Stein, and Qaim 2018). A major cause of trace element malnutrition results is the growth of crops on infertile soils with poor phyto-availability of micronutrients for human nutrition (Barrett and Bevis 2015; Sahn 2015; Oliver and Gregory 2015; White and Brown 2010), Such declining soil fertility can be caused by natural soil erosion and the widespread dependency of conventional ‘Green Revolution’ agricultural methods, which involve the application of chemical (N, P, K) fertilisers, genetically modified crops, water management and intense cropping regimes (Godfray et al. 2010a; Foley, Ramankutty, Brauman, Cassidy, Gerber, Johnston, Mueller, O’Connell, et al. 2011; Tilman et al. 2011; Godfray and Garnett 2014). Soil mineral depletion on agricultural land is now critical, such that 51 % and 30 % of global crop land is deficient in Zn and Fe respectively (White and Zasoski 1999). The UN Decade of Action on Nutrition (2016 – 2025) is attempting to address micronutrient mineral malnutrition and hidden hunger against the backdrop of the UN 2030 Sustainable Development Goals, most via notably Goal 2 “End hunger, achieve food security and improved nutrition and promote sustainable agriculture” (Organization 2018).

While agricultural intensification is one cause of micronutrient deficiency in crops, food security projections suggest that we will be unable to meet food demands against the backdrop of climate uncertainty without agricultural land expansion, necessitating cultivation of regions that were once unsuitable for crop growth, such as deglaciating landscapes at high latitude or high-altitude areas (Zimmer et al. 2017). The potential impact of such expansion upon the TE remobilisation from soils to crops at harmful levels poses a potential threat to food security and human health, but has not been widely evaluated (Clemens and Ma 2016). These virgin land surfaces are likely to have high concentrations of heavy species (e.g. As, Cd, Cr, Ni, Pb, Zn) similar to contaminated agricultural soils which are known to be the largest source of heavy metals to humans, resulting in a growing necessity for trace element management, remediation and mitigation (Gall, Boyd, and Rajakaruna 2015).

TE consumption above the recommended maximum dose has been shown to have acute and chronic toxicity to human health. Toxicity can be carcinogenic (As, Cd, Co, Cr, Ni, Pb, Se) (Türkdoğan et al. 2003), neurotoxic (e.g. Mn toxicity as a causative agent in Parkinson's syndrome (Goldhaber 2003)), teratogenic (in utero exposure to As, Cd, Ni and Pb increases the risk of orofacial clefts in newborns (Ni et al. 2018)) and can cause endocrine disruption (e.g. As, Hg and Pb exposure may result in female subfertility or infertility (Rattan et al. 2017)). Additionally, sub-chronic exposure can be pernicious to human health, suppressing immune system function, increasing underlying illness across whole populations (Jadhav et al. 2007). However, many of these toxic heavy metals are economically valuable elements (e.g. Ni), and their extraction from toxic heavy metal rich soils, 'agromining', using corresponding hyperaccumulating crops (e.g. *Phyllanthus rufuschaneyi*) is gaining traction as a future tool to meet global demands whilst reducing the impact of mining and remediating toxic soils (Baker et al. 2020).

Improving crop micronutrient status under agricultural intensification, whilst minimising potentially harmful effects of toxic metal bioaccumulation as new land surfaces are cultivated, demands effective strategies which work synergistically between crop growth and soil processes. The application of crushed rock has been heralded as one such strategy, where the crushed rock chemically weathers, restoring limited soil macronutrient (P, K, Ca, Mg, S) content (Hensel 1894b), whilst improving soil properties, crop yields, plant growth and CO_2 uptake via enhanced weathering (Bakken et al. 2000; Basak, Sarkar, and Naidu 2020; Gillman 1980; Mohammed et al. 2014; Priyono et al. 2020; Priyono and Gilkes 2008b; Ramos, de Mello, and Kautzmann 2014; Coroneos, Hinsinger, and Gilkes 1996; Van Straaten 2006b; Guelfi-Silva et al. 2013; Silva et al. 2014; Bolland and Baker 2000b). Past research has focused on the use of waste rock dust from mining and cement manufacturing, highlighting concerns over high concentrations of ores and heavy toxic metals (e.g. Cr, Ni and Pb), however, the potential for beneficial TE biofortification of crops has not been assessed (e.g. Sr and Zn) (Beerling et al. 2018a; Vitó et al. 2020; Kelland et al. 2020).

A novel alternative strategy to crushed rock is glacial flour, a source of naturally crushed rock, which proposes a holistic soil treatment with positive benefit for crops (Chapter 4 of this thesis), (Sukstorf, Bennike, and Elberling 2020). Glacial flour is composed of reactive fine particles (< 66 μm) generated by glacial erosion and conveyed by meltwaters to major rivers at concentrations of 0.1 g L^{-1} - 1 g L^{-1} (Brown, Tranter, and Sharp 1996a; Wulf, Bookhagen, and Scherler 2012; Srivastava et al. 2014; Singh, Ramanathan, and Pottakkal 2016a; Singh and Ramanathan 2018, 2015; Singh et al. 2003; Hodgkins et al. 2003; Cowan and Powell 1990). Glacial flour can be rich in macronutrients (P, K) and TEs (such Mn and Zn) which are important for biological productivity, but can include potentially toxic heavy species (e.g. As, Cd, Co, Cr, Hg, Ni, Pb, Se) in some bedrock terrains (Hawkings et al. 2015a; Hawkings, Skidmore, Wadham, Priscu, Morton, Hatton, Gardner, Kohler, Stibal, Bagshaw, et al. 2020; Hawkings et al. 2016; Hawkings et al. 2017; Hawkings et al. 2014; Hawkings et al. 2021). Evaluation of the potential of glacial flour application on TE bio-accumulation in crops has high relevance in the context of zero-budget micronutrient soil improvement strategies (Shiferaw, Okello, and Reddy 2009; Altieri and Nicholls 2012; Gomiero, Pimentel, and Paoletti 2011; Food and Agriculture Organization 2015; DeLonge, Miles, and Carlisle 2016; Mayer, Pfeiffer, and Beyer 2008; Ramakrishnan 2002a), and has the potential to yield critical insights into crop TE status with the expansion of agricultural land to high mountain areas as glaciers retreat and growing seasons lengthen. The impact of farming these relatively un-weathered soils on the potential uptake of macronutrients and TE by crops is unknown (Arndt et al. 2019; Drever 1994).

This study is the first controlled crop growth experiment aimed at investigating the uptake of macro-nutrient and trace element in glacial flours by the legume, soybean (Glycine max. var. Black jet). Soybeans are a widely cultivated crop, important throughout the Global South (Das et al. 2018). The use of a legume eliminates the need for N fertilisation, given the low N content of most glacial flours, which is supplied via the symbiotic relationship between a legume and root rhizobia (Ledgard and Steele 1992). We employed glacial flours sourced from two glaciated mountain regions: Sólheimajökull glacier, Iceland (63.4 N, 19.4 W) dominated by flood basalts (Carswell 1983); and Himalayan glacial flour from Chhota Shigri glacier, India (32.3 N, 77.7 E), composed of igneous / metamorphic gneiss and granites with minor sedimentary bands (Singh et al. 2015). Glacial flour was applied at increasing doses (0.5, 1, 2, 5, 10, and 20 T ha^{-1}) to simulate proposed application rates recommended for crushed rock to soils (Manning 2010; Lewis et al. 2021; Beerling et al. 2018a; Beerling et al. 2020; Kantola et al. 2017), the results were compared to a control and NPK chemical fertiliser treatment. Trace element (TE) and nutrient concentrations were determined in both the glacial flours and the soybean crop, using an adapted total metal extraction method (Tessier, Campbell, and Bisson 1979b). We focus specifically on the uptake of plant macronutrients (Ca, Mg, Fe, S, P and K) to infer potential in-soil chemical weathering processes, as well as the bioaccumulation of a range of TEs (As, Mo, Sr, Zn, Se and Mn) in the soybean crop.

5.3 Material and Methods

5.3.1 Glacial flour sampling

Glacial flours, recently deposited on river banks of glacial meltwater rivers, were collected from two glacier field sites: Sólheimajökull Iceland (63.4 N, 19.4 W) in October 2016 and Chhota Shigri glacier, Hindu Kush Himalaya, India (32.3 N, 77.7 E) in September 2017. Glacial flour was collected at both sites ~10 m from the glacial outflow portal using a plastic trowel which was cleaned between uses using MQ water. After collection, glacial flour samples were stored in sterile Whirl-Pak® bags under refrigerated (4 °C). All analyses were conducted on the flours up to 6 months after collection.

5.3.2 Soybean plant growth

Soybean TE uptake experiments were carried out using glass house pot trails (Mohammed et al. 2014). An artificial soil matrix was used to mimic impoverished soils and to best reveal glacial flour impacts on the soil nutrient status, which was composed by volume of 90 % perlite (Silvaperl P35 Grade, Hoben International, Westland Horticulture, UK) and 10 % compost (50:50 mix of Silver Sand, Melcourt and Levington® John Innes No 2). Pot cation exchange capacity was calculated by using manufacturer information. The elemental composition of the artificial soil matrix is displayed in Table 5.1. Both glacial flours were added to the artificial soil matrix by homogenously mixing all components in a clean zip lock bag, before filling the pot, and flour additions were controlled to achieve applications rates of 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 T ha^{-1}. The latter were calculated based on the surface area of the pot (19 cm^2) assuming a 10 cm soil depth in a 12 cm-tall pot. In addition to the glacial flour-treated pots, chemical fertiliser-amended and control (no glacial flour or chemical fertiliser addition) pots were also prepared. All chemical fertilisers were mixed in the laboratory using acid washed glassware and MQ, comprising of N via Ammonium nitrate, NH_4NO_3, P via P_2O_5 and K via K_2O, all reagents used were analytical grade with concentrations of < 0.5 ppb heavy metal species.. Chemical P, K and N were applied at 10 kg ha^{-1} based on recommended minimum low-rate fertiliser rates (Roy et al. 2006).

Soybean seeds were stratified (cold-treated) for 3 days at 4 °C before being sown into vermiculite (Sinclair Pro, Medium, www.sinclairpro.com) and propagated at 25 °C and 100 % humidity until chitting was visible (5 – 8 days). Following germination, the roots of the soybean seedlings were inoculated with a microbial inoculum, (*Bradyrhizobium japonicum*), (Legume Fix, Legume Technology, UK). Soybean seedlings were than transplanted into their treated pots and the plants grown in controlled environment GroDome chambers (Unigro) with 50 % humidity, 20 ºC temperature and a 12:12 hour light: dark photoperiod, supplied by sunlight supplemented by 80 W m^{-2} overhead lighting (<206 W Attis7 LED grow lamps). Plants were watered by hand (from above) with RO water to maintain optimal moisture conditions whilst minimising any nutrient additions. 100 mL of RO water was added to the top of the pot every 7 days (Mohammed et al. 2014). Each 12 cm pot was labelled with a 5 digit code and arranged in a randomized design on an individual tray to prevent transfer or loss of water or nutrients (Manning et al. 2017). The beans and plants were harvested 12 weeks after planting, the above ground biomass was removed, and the bean seeds and plant biomass placed in separate paper trays and oven dried at 65 °C for 4 days prior to being weighed for bean mass (mg), total plant biomass (mg) and trace element extractions.

Soybean biomass (mg) was determined by oven drying (24 hrs at 150 °C) the unshelled soybean seeds for 12 hours and then weighing immediately. To compare soybean enrichment across experimental treatments the TE concentration (mg g^{-1}) data from extractions and the TE uptake (mg) was used. TE uptake was calculated using the soybean biomass (mg) and the trace element concentrations (mg g^{-1}) from the extractions above.

Table 5.1: Artificial soil matrix component elements. Values shown to 3 significant figures. Error is the standard deviation for 3 replicates.

Soil properties	Perlite	Compost

Total P (Exchangeable P)		
Dry sediment (µg g^{-1})	< LOD	104 (18.2)
Total K (Exchangeable K)		
Dry sediment (µg g^{-1})	312 (55.5)	176 (27.4)
Total S (µg g^{-1})	< LOD	217
Total Fe (Exchangeable Fe) (µg g^{-1})	239 ± 5 (55.5 ± 2.0)	151 ± 19 (27.4 ± 1.8)
Total Zn (µg g^{-1})	27.8 ± 3.5	6.71 ± 1.46
Total Ca (µg g^{-1})	752 ± 55	3510 ± 265
Total Mg (µg g^{-1})	887 ± 83	72.4 ± 4.6
pH (2 significant figures)	7.4	5.4
Soil moisture (%)	0.76	76.3
Loss on Ignition (%)	0.30	97.2

5.3.3 Trace element extraction and analysis

Prior to extraction for TEs, all dried plant and sediment samples were milled by hand in a pre-cleaned ceramic pestle and mortar to avoid contamination. All pestle and mortars, glassware, LDPE 15 mL sample bottles, polypropylene / polyethylene [PP/PE] syringes and pipette tips were cleaned sequentially using 1 % Decon 90 (24 hours), 6 M HCl (48 hours) and 3 M HNO3 (48 hours), with at least six rinses with MQ between each wash before drying in the laminar flow hood (Hawkings, Skidmore, Wadham, Priscu, Morton, Hatton, Gardner, Kohler, Stibal, Bagshaw, et al. 2020). Whatman GD/XP PES (polyethersulfone) 0.45 um syringe filters were used for extracting the exchangeable fraction supernatant, these were cleaned using ultra trace metal grade HCl, passing 20 mL of 1.2 M HCl, with the final 1 mL left in the filter for approximately 2 hours before rinsing with 40 mL of MQ and flushing with laminar flow filtered air to dry as described in Hawkings et al. (2014).

The extraction method for plant and sediment samples was the same. The total element and TEs (P, K, Fe, Ca, Mg, Mn, S, Se, Zn, As) were extracted from the mineral and bean samples using a modified aqua regia digest. For each digestion, 0.1 - 0.5 g of sample was added to 2 mL of 30 % hydrogen peroxide, 2.5 mL of 37 % hydrochloric acid and 10 ml of 67 % nitric acid (Sigma). This extraction solution was then digested in a Mars 6 microwave in pressurized Teflon vessels, (US EPA 3051A). The temperature was increased to 210^0 C over 20 mins, then held constant for 15 min. After a 10x dilution with 0.1 M HNO_3, the extraction solutions were filtered through Whatman grade 41 GF/F filter papers and then 5x diluted with 0.1 M HNO_3 to a total of 50 mL prior to analysis. Elemental and TM concentrations (P, K, Fe, Ca, Mg, Mn, S, Se, Zn, As) in the extraction solution were determined by an Agilent 7500 inductive coupled plasma mass spectrometer, ICP-MS (Newcastle University). The precision of these analyses was: P ±2.6 %; K ±2.9 %; Fe ± 0.8 %; Ca ±5.9 %; Mg ±2.6 %; Mn ±2.2 %; S ±9.1 %; Se ±1.9 %; Zn ±1.9 %; As ±2.2 %. Accuracy for each element was: P +0.2 %; K +2.5 %; Fe +1.1 %; Ca +0.4 %; Mg +3.8 %; Mn +0.7 %; S +4.1 %; Se +11.1 %; Zn +6.6 %; and As +6.7 %; based on repeated mid-range standards.

To ensure we could determine S % in the case that glacial flour S content was low, elemental analysis was performed. Firstly, gravimetric soil moisture was determined, followed by oven drying glacial flour (24 hrs at 150 °C), after which flours were pulverised with a pestle and mortar (<1 mm) and ~ 10 mg subsamples were weighed in triplicate into tin capsules. These capsuled samples were then analysed for the S contents using an elemental analyser (vario PYRO cube; Elementar Analysensysteme GmbH, Hanau, Germany). The elemental analyser was calibrated with sulfanilamide (S:18.62 %) and the precision as a relative standard deviation (RSD) was < 5 %. LOD was 0.001 % S.

Phosphorous was sequentially extracted from the glacial flours investigated using the methods from Stibal et al. (2008) and Hawkings et al. (2016). This sequential extraction method removes decreasingly reactive defined fractions of P. Extraction 1 removes loosely sorbed P using 1 M $MgCl_2$ solution. Extraction 2 uses 0.1 M NaOH removes Fe– and Al–bound P that is believed to be potentially biolabile (NaOH-P), the sum of these two fractions is termed 'Labile-P'. Extraction 3 removes Ca- and Mg- bound P, which is less reactive using HCl (HCl-P). The final extraction, extraction 4 determines the 'residual' and organic bound P (Res-P) through a potassium persulfate / sulfuric acid digest. Concentrations of the resulting extracts were determined colourimetrically on a LaChat QuikChem® 8500 series 2 flow injection analyser (QuikChem method 31-115-01-1-I). Precision was ±0.5 %, ±0.4 %, ± 0.2 % and accuracy was -0.5 %, +0.3 %, +1.4 % based on six replicate standards for extractions 1, 2, 3.

5.3.4 Data analysis

Dose response depletion and the enrichment of TMs in the Soybeans were determined using linear regression between the bean concentration ($\log_{10}y$) and the glacial flour or chemical fertiliser application rate ($\log_{10}x$). The gradient of the line ($y = ax^k$), 'k' was used to indicate a positive or negative response, and tested for statistical significance, using R^2 values and p-values. Statistical analysis was performed using R Core Team (2013), R: A language and environment for statistical computer, R foundation for Statistical Computing, Vienna, Austria (www.R-project.org). Results were assessed for normal distribution and used in this analysis if considered significant if p-values were < 0.05.

To enable comparisons between the soybeans grown in this experiment and soybeans from in real world agriculture, we compared our experimental TE concentrations with the TE concentration of the typical agricultural soybean, termed the 'Standard Soybean'. The Standard Soybean TE concentrations are derived from those reported by O'Dell (1979) and Liu (1997) and are employed within worldwide nutritional guidance (Organization 1996).

5.3.5 Soil enrichment assessment

Pot TE concentrations (ug g^{-1}) were calculated using the combined total extractable elements from the perlite, compost artificial matrix and addition of glacial flour. The TE in the pot soils were then compared to the Indian standard (2000) and EU soil quality (2021) parameters which are the most applicable statistics for our glacial flours sourced (Bünemann et al. 2018; Kumar et al. 2019).

5.3.6 Soybean nutrition and contamination indices

Total concentrations of elements (Ca, Fe, K, Mg, Mn, Mo, P, S, Se, Sr and Zn) within a human dietary context are either termed beneficial macronutrients (Ca, Fe, K, Mg, P, S) whereby recommended consumption is > 250 ug per day, or beneficial micronutrients (Mn, Mo, Se, Sr and Zn) where recommended consumption is < 100 ug per day (Organization 2003). Elements regarded as TEs in this experiment (As, Cd, Co, Cr, Cu, Ni, Pb and Zn) are those that can be beneficial at low levels, but also detrimental to human health, either via acute or chronic toxicity when consumed at higher levels (Organization 2003). To determine the potential toxic impact of TE consumption from the soybeans in this experiment we utilised several frequently-applied measures and indices.

First, the TE concentration of the soybean was compared to the Indian Standard (2000), FAO Codex International standards (2013) and EU standards (2012), acting as a measure of imminent toxic concern to health. The concentrations were used for both toxic and beneficial elements to calculate consumption of TE (ug) for a 75 g portion of unshelled raw wet soybeans. Each portion was calculated at 75 g, which falls within the range of raw uncooked un-shelled beans as recommended by the WHO, at 58.4 – 87.5 g (1/3 – ½ cup) (Banaszkiewicz 2011). Since the TE extractions on the soybeans were performed after oven drying, we weighed soybeans before and after drying to calculate the wet portion mass (g) from the dry soybean equivalent mass (g), which was approximately 25 g dry weight equivalent (25 g). TE consumption of the experimental soybeans was compared to both the recommended daily intake reference value (DIRV) (FAO Codex 2013) or the Daily intake limit (FAO / WHO 2017) to indicate dietary enrichment or toxicity.

Second, Metal Pollution Index (MPI) was employed to analyse the potential risk associated with all potentially toxic TE. The TE species typically included in the calculation of MPI vary throughout the literature, and we focus here on TEs that could become toxic for human health if present in high doses (As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Se, Sr and Zn) (Zhang et al. 2014; Singh et al. 2010; Kumar, Shukla, et al. 2020). TE extractions showed that Total Cd, Co, Cr, Cu and Pb for all soybeans were < LOD, and Hg was not measured, therefore MPI was determined using concentrations of As, Fe, Mn, Mo, Se, Sr and Zn. In this investigation, only the TE (As, Fe, Mn, Mo, Se, Sr and Zn) that were above the LOD were used to assess multi-element toxicity. MPI was calculated using Equation 5.1.

$$MPI = (Cf_1 \text{ x } Cf_2 \text{ x } \ldots. \ Cf_n)^{1/n} \qquad \text{(Equation 5.1)}$$

where, Cf is the concentration (ug g^{-1}) of each TE in the soybean and n was the number of TE species, with a total of 7 TEs (i.e., Cf_1-Cf_7) e.g. (Cf_1 = Total Fe, Cf_2 = Total Zn) etc. An MPI > 100 is deemed critically polluted (Kumar, Shukla, et al. 2020).

Third, Health Risk Indices (HRI) were utilised to assess potential chronic exposure to toxic TEs. HRIs are commonly used in land remediation, particularly from contaminated land (e.g. via mining) and conversion to agricultural land in India and China (USEPA 2021). The HRI was calculated for each TE in the soybean and is based upon the ratio of exposure of glacial flour-treated crops represented by the Daily Intake of Metal (DIM), calculated by

Equation 5.2, and the chronic oral reference dose for each element, where the exposure time is 7 years (approximately 10 % of a human life time) (Table 5.2) (USEPA 2021). HRI was calculated as follows in Equation 5.2 and 5.3:

Daily intake of metal (DIM) =

$$\frac{C_{TE} \times D_{\text{food intake}}}{B_{\text{average weight}}} \quad \text{(Equation 5.2)}$$

Health Risk Index (HRI)=

$$\frac{\text{DIM}}{\text{Oral reference dose ((mg / kg) day}^{-1}\text{)}} \quad \text{(Equation 5.3)}$$

where, C_{TE} is the concentration (ug g^{-1}) of the specific TE in the soybean, $D_{foodintake}$ is the WHO recommended daily portion of dried soybeans at 25 g, and $B_{averageweight}$ is based upon an average weight survey of adults in India, assumed to be 60 kg (Dhillon et al. 2016).

A HRI of > 1 suggests a crop which is not safe for human consumption (USEPA 2021). To compare our glacial flour-treated soybeans to soybeans grown typically across the world, we also used the standard TE concentrations of a typical soybean concentration, with balanced dietary elemental intake and calculated the HRI for TE consumed from these beans. The typical soybean concentrations are based upon well-defined trace element concentrations used throughout literature, and included within the results tables for comparison (O'Dell 1979).

Table 5.2: Oral reference doses (RfD) of trace elements and reference source

Element	RfD *(µg / kg day^{-1})*	Reference
As	3.0	World Health Organization (2022)
Fe	48,000	World Health Organization (2022)
Mn	0.14	Organization (2011)
Mo	25	Organization (2011)
Se	300	World Health Organization (2022)

Sr	25	World Health Organization (2022)
Zn	300	World Health Organization (2022)

5.4 Results

5.4.1 Glacial flour macronutrient and TE content

Concentrations of macroelements and TE within both glacial flours are presented (Table 5.4 and Table 5.5). The Total P and Total K content for Himalaya and Icelandic flour were within a similar range (Total P: Himalaya 2.24 ± 0.1 mg g^{-1}, Iceland 2.85 ± 0.04 mg g^{-1}; Total K: Himalaya 8.41 ± 0.26 mg g^{-1}, Iceland 6.76 ± 0.15 mg g^{-1}). The sequential P extractions indicate that > 95 % of Total P in both glacial flours was held in the carbonate-mineral bound phase (Table 5.3).

The two flours showed distinct differences in concentrations of other elements. Firstly, Icelandic flour was more enriched in macronutrients (Total-Ca, Total-Mg, and Total-S) and micronutrients (Total-Fe 152 ± 3 mg g^{-1}; Total Zn 232 ± 2 ug g^{-1}; Total Ni 86.9 ± 2.9 ug g^{-1}) compared with Himalaya flour (Total Fe 20.5 ± 0.2 mg g^{-1}; Total Zn 114 ± 3.1 ug g^{-1}; Total Ni 12.8 ± 0.2 ug g^{-1}) (Table 5.4). Total Mo was below the LOD for both glacial flours. Both glacial flours also contained measurable potentially toxic TE (As, Cd, Co, Cr, Cu, Pb and Se) (Table 5.5). Using the TE concentration data of all soil matrix components (Table 5.1) and the glacial flours, we determined that TE concentrations in the pot were within the maximum permissible TE limits for Indian and EU agriculture for all Icelandic flour treatments (Table 5.6). Himalayan flour treatments were within permission TE limits for all TE apart from As (Table 5.6). The concentration of Total As in Himalayan flour treated pots at 10 T ha^{-1} and 20 T ha^{-1} was 6.43 ± 0.85 ug g^{-1} and 12.4 ± 1.10 ug g^{-1} respectively, exceeding all permissible soil limits; EU Standards (2012) 0.15 ug g^{-1}, FAO Codex (2013) 0.1 ug g^{-1} and Indian Standard soil limits (2000) 1.1 ug g^{-1}.

5.4.2 Glacial flour enhanced macronutrient and TE in soybean crop

Glacial flour applied at a dose practical for application by farmers (2 T ha^{-1}), a rate which was based upon agricultural liming and prior crushed rock research, enriched soybean elemental concentrations above the above the control and NPK fertiliser treatments (Figure 5.1A, Table 5.7, 5.8) (van Straaten 2006a; Manning and Theodoro 2020). Glacial flour (2 T ha^{-1}) treated soybeans were enriched in all investigated macronutrients (P, K, Mg, Ca and S) (Figure 5.1B, Table 5.7) and showed a clear enrichment of TE (As, Mo, Sr, Zn, Se, Mn) compared to the typical agricultural soybean, (Figure 5.1A, 1B). Icelandic flour (2 T ha^{-1}) enriched TEs (Mo, Sr, Se, Mn, Fe) and macronutrients (Ca, Mg) significantly above Himalayan flour at 2 T ha^{-1} ($p < 0.05$). The macronutrient and TE concentrations of the control treatment were within the normal range for typical agricultural soybeans (Figure 5.1B).

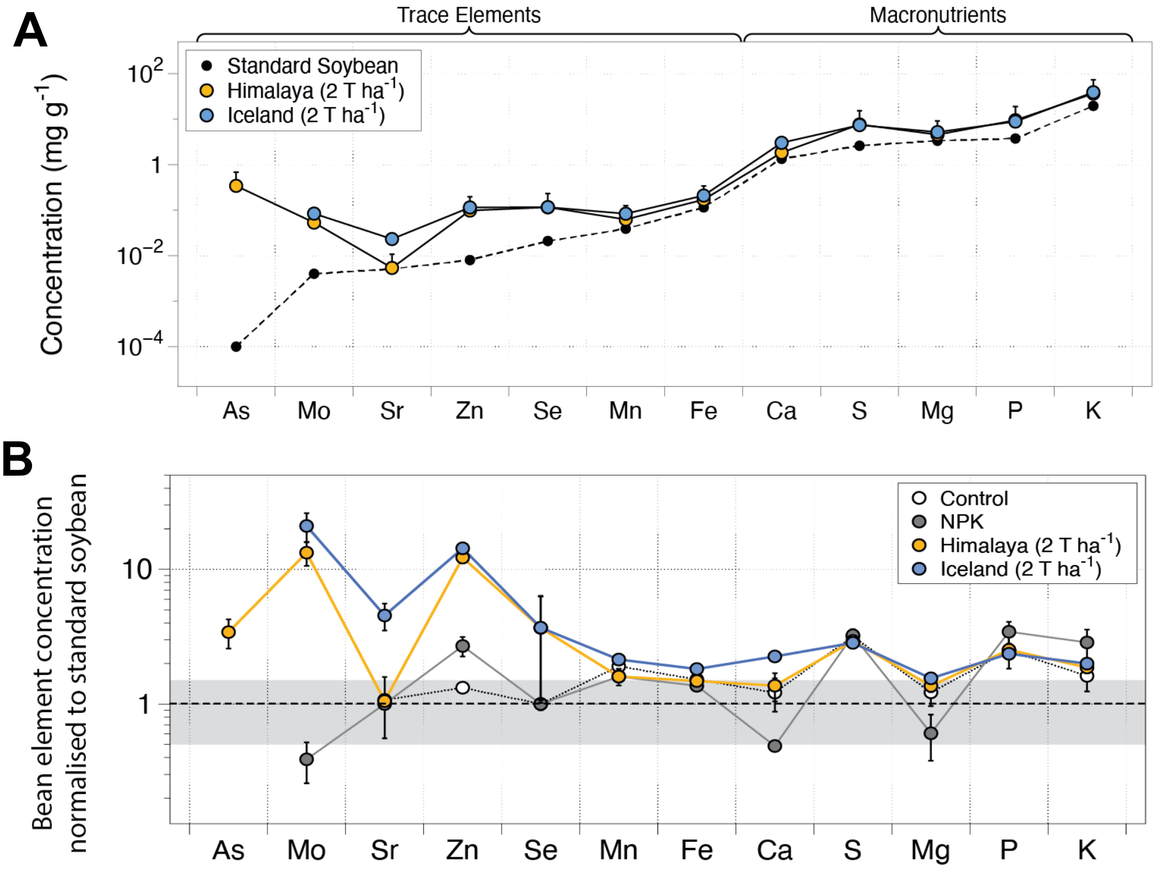

Figure 5.1, A) Soybean total elemental concentrations for the standard soybean (ranked low to high), and for Himalayan and Icelandic flour applied at 2 T ha^{-1}. **B)** Soybean element concentration in pot treatments using glacial flour at 2 T ha^{-1}, controls and NPK fertiliser, all standardised to the typical agricultural soybean elemental standard concentration (O'Dell 1979). Error bars on both figures represent standard deviation of three replicates per treatment.

1.0 ± 50 %, grey shaded area) and soybeans grown with the addition of chemical fertiliser alone were significantly depleted (< 50 % of the typical soybean) in Mo and enriched in Zn, S, P and K (> 50 % of the typical soybean) (Figure 5.1B, Table 5.7). Notably, NPK treated soybeans displayed significantly lower concentrations of Mo, Zn, Se, Ca and Mg compared to both the glacial flour treatments ($p < 0.05$) and the control (Figure 5.1B, Table 5.7).

The results when glacial flour was applied at a range of doses (0 – 20 T ha^{-1}) indicate that soybeans treated with glacial flour achieved greater biomass than the control and low rate (10 kg ha^{-1}) NPK fertiliser (Chapter 4). Soybean biomass displayed a strong positive correlation with glacial flour application rate ($R^2 = 0.82$, $p < 0.05$) (Chapter 4), demonstrating an influence of flour-derived nutrients on crop growth. To support plant greater biomass, plants require a greater uptake of nutrients, placing further demands on nutrient supplies (Khan et al. 2015). Elemental extraction data from the soybeans suggests that elements fall into one of four groups based on their concentration (mg g^{-1}) and uptake (mg).

Table 5.3: Sequential Phosphorous extraction data for Himalayan and Icelandic glacial flours on uncrushed, dry glacial flour. Data is presented to 3 significant figures or 1 decimal place. HCl-P forms 99 % and 97 % of P in uncrushed Himalayan and Icelandic flour respectively. Exchangeable P (MgCl-P + NaOH-P) is 0.8 % and 2.5 % of Himalayan and Icelandic flour in uncrushed rock.

	MgCl-P	NaOH-P	HCl-P	Res-P / POP	Total P (uncrushed)	Total P (crushed)	n
Flour				*(µg g^{-1} (Dry sediment))*			
Himalaya	1.2 ± 0.5	4.4 ± 2.7	724 ± 52	3.1 ± 2.6	733 ± 61	[2240 ± 10]	9 [3]
Iceland	9.8 ± 0.6	14.8 ± 5.4	953 ± 80	5.2 ± 2.1	983 ± 95	[2850 ± 40]	9 [3]

Table 5.4: Measured mean glacial flour concentrations of plant essential exchangeable (uncrushed, labile extractions) and total nutrients (crushed, total extraction). Also showing the % S from Elemental Analysis. Values from this study are presented to three significant figures.

	Total-P (Exch-P)	**Total-K (Exch-K)**	**Total-Fe (Exch-Fe)**	**Total-Ca**	**Total-Mg**	**Total-Mn**	**Total-S**	**Total-Zn**	**Total-Ni**	**S**
				($mg\ g^{-1}$)				*($ug\ g^{-1}$)*		*(%)*
Sólheimajökull Glacier, Iceland 'Icelandic flour'	2.85 ± 0.04 (0.024 ± 0.003)	6.76 ± 0.15 (1.07 ± 0.09)	152 ± 3 (4.05 ± 0.08)	27.4 ± 0.08	33.5 ± 0.09	2.50 ± 0.04	3.56 ± 0.04	232 ± 2.2	86.9 ± 2.9	
Chotta Shigri Glacier, Himalaya 'Himalayan flour'	2.24 ± 0.10 (0.006 ± 0.001)	8.41 ± 0.26 (0.38 ± 0.07)	20.5 ± 0.2 (1.49 ± 0.02)	2.35 ± 0.06	3.47 ± 0.06	< LOD	< LOD	114 ± 3.1	12.8 ± 0.2	

Table 5.5: Measured mean glacial flour concentrations of plant non-essential total nutrients (crushed, total extraction) Values from this study are presented to three significant figures.

	Total-As	**Total Cr**	**Total Co**	**Total Pb**	**Total Se**
			(ug g^{-1})		
Sólheimajökull Glacier, Iceland ‘Icelandic flour’	2.59 ± 0.03	33.7 ± 0.9	70.3 ± 1.5	3.71 ± 0.08	6.01 ± 0.25
Chotta Shigri Glacier, Himalaya ‘Himalayan flour’	73.8 ± 8.0	12.9 ± 2.1	5.79 ± 0.07	8.70 ± 0.25	3.49 ± 0.47

Table 5.6: Total TE concentrations within the pot experiment soils, alongside the maximum permissible levels of TE in soils for different relevant agencies. Data in bold indicates where a pot treatment has exceeded a given soil maximum permissible elemental limit. Data is presented to 3 significant figures.

		As	Cd	Co	Cr	Cu	Fe
				(ug g^{-1})			
Indian Standard 2000		**20**	**3 - 6**		**124**	**135 - 270**	**-**
EU Standards 2013		**5**	**3**	**100**	**150**	**140**	**-**
Control pot		BDL	0.50 ± 0.07	0.50 ± 0.05	1.40 ± 0.31	2.40 ± 0.50	230 ± 44
NPK fertiliser		BDL	0.49 ± 0.07	0.50 ± 0.05	1.40 ± 0.31	2.40 ± 0.50	230 ± 44
Himalaya Flour (T ha^{-1})	0.5	0.35 ± 0.02	0.50 ± 0.09	0.52 ± 0.08	1.45 ± 0.28	2.42 ± 0.50	326 ± 35
	1	0.67 ± 0.10	0.50 ± 0.11	0.55 ± 0.09	1.50 ± 0.26	2.44 ± 0.46	413 ± 42
	2	1.17 ± 0.31	0.49 ± 0.08	0.58 ± 0.10	1.58 ± 0.25	2.46 ± 0.44	547 ± 63
	5	3.17 ± 0.27	0.49 ± 0.10	0.72 ± 0.21	1.88 ± 0.29	2.57 ± 0.52	1070 ± 48
	10	**6.43** ± 0.85	0.47 ± 0.09	0.92 ± 0.18	2.33 ± 0.34	2.73 ± 0.53	1860 ± 112
	20	**12.4** ± 1.10	0.45 ± 0.15	1.26 ± 0.32	3.06 ± 0.38	2.99 ± 0.61	3150 ± 189
Iceland Flour (T ha^{-1})	0.5	0.01 ± 0.001	0.50 ± 0.08	0.80 ± 0.24	1.54 ± 0.29	2.62 ± 0.42	888 ± 52
	1	0.02 ± 0.001	0.51 ± 0.12	1.11 ± 0.21	1.68 ± 0.44	2.84 ± 0.51	1560 ± 115
	2	0.04 ± 0.002	0.52 ± 0.14	1.67 ± 0.18	1.94 ± 0.22	3.25 ± 0.31	2770 ± 127
	5	0.09 ± 0.01	0.53 ± 0.09	2.79 ± 0.27	2.45 ± 0.30	4.05 ± 0.74	5240 ± 188
	10	0.22 ± 0.03	0.57 ± 0.11	5.91 ± 0.68	3.90 ± 0.79	6.33 ± 1.20	12000 ± 200
	20	0.44 ± 0.01	0.64 ± 0.14	10.6 ± 0.87	6.08 ± 0.95	9.77 ± 1.36	22300 ± 265

Table 5.6 (Continued): Total TE concentrations within the pot experiment soils, alongside the maximum permissible levels of TE in soils for different relevant agencies. Data in bold indicates where a pot treatment has exceeded a given soil maximum permissible elemental limit. Data is presented to 3 significant figures.

		Mn	Mo	Ni	Pb *(ug g^{-1})*	Se	Sr	Zn
Indian Standard 2000		**-**		**75 - 150**	**250 - 500**	**10**		**300 - 600**
EU Standards 2013		**-**		**75**	**300**		**465**	**300**
Control pot		43.6 ± 2.5	0.15 ± 0.01	4.62 ± 0.16	3.72 ± 0.31	1.15 ± 0.41	2.87 ± 0.89	10.3 ± 1.12
NPK fertiliser		43.6 ± 2.5	0.15 ± 0.01	4.62 ± 0.16	3.72 ± 0.31	1.15 ± 0.41	2.87 ± 0.89	10.3 ± 1.12
Himalaya Flour (T ha^{-1})	0.5	44.1 ± 2.8	0.15 ± 0.01	4.66 ± 0.15	3.74 ± 0.33	1.16 ± 0.38	2.86 ± 0.88	10.8 ± 1.12
	1	44.5 ± 2.6	0.15 ± 0.01	4.69 ± 0.17	3.76 ± 0.33	1.17 ± 0.51	2.85 ± 0.93	11.3 ± 1.16
	2	45.3 ± 3.1	0.15 ± 0.01	4.75 ± 0.16	3.80 ± 0.32	1.19 ± 0.61	2.83 ± 0.90	11.9 ± 1.17
	5	48.1 ± 3.6	0.16 ± 0.01	4.96 ± 0.18	3.93 ± 0.35	1.25 ± 0.55	2.78 ± 0.88	14.6 ± 1.23
	10	52.4 ± 3.2	0.17 ± 0.02	5.27 ± 0.21	4.12 ± 0.39	1.34 ± 0.63	2.69 ± 0.95	18.6 ± 1.36
	20	59.3 ± 2.9	0.19 ± 0.01	5.79 ± 0.23	4.44 ± 0.41	1.49 ± 0.58	2.54 ± 0.96	25.2 ± 1.45
Iceland Flour (T ha^{-1})	0.5	54.2 ± 3.8	0.15 ± 0.01	4.97 ± 0.18	3.72 ± 0.31	1.17 ± 0.52	4.78 ± 1.35	11.3 ± 1.15
	1	65.1 ± 5.6	0.15 ± 0.01	5.34 ± 0.22	3.72 ± 0.31	1.19 ± 0.55	6.74 ± 1.73	12.3 ± 1.21
	2	84.7 ± 4.5	0.15 ± 0.02	6.00 ± 0.19	3.72 ± 0.32	1.23 ± 0.60	10.2 ± 1.80	14.0 ± 1.27
	5	124 ± 5.5	0.16 ± 0.01	7.29 ± 0.24	3.69 ± 0.34	1.30 ± 0.59	17.4 ± 2.22	17.5 ± 1.33
	10	234 ± 6.3	0.18 ± 0.01	11.0 ± 1.20	3.71 ± 0.28	1.52 ± 0.57	37.1 ± 4.86	27.5 ± 1.50
	20	400 ± 10.0	0.22 ± 0.02	16.6 ± 1.24	3.72 ± 0.29	1.86 ± 0.62	66.9 ± 5.03	42.5± 2.20

Table 5.7: Plant Toxic TE concentrations (ug g^{-1}) soybean glacial flour treatments from this crop growth experiment alongside maximum permissible limits and the typical 'standard' soybean concentrations. Values in bold are over permissible limits. Methodological limit of detection (LOD) also shown for all elements, values below the detection limit are indicated as BDL. Values in brackets are single replicate results only. Data is presented to 3 significant figures.

		As	Cd	Co	Cr	Cu	Ni	Pb	Zn
					(ug g^{-1})				
Indian Standard (2000)		1.1	1.50	-	20.0	30.0	1.50	2.50	50.0
FAO Codex (2013)		0.1	0.10	-	-	40.0	-	0.10	60.0
EU Standards (2012)		0.15	0.20	1.6	-	-	-	0.30	-
Typical Bean		0.01	0.01	0.00	0.01	0.00	0.00	0.00	8.00
Control		BDL	BDL	BDL	BDL	BDL	BDL	BDL	**73.2 ± 5.2**
NPK fertiliser		BDL	BDL	BDL	BDL	BDL	BDL	BDL	**41.2 ± 8.9**
Himalaya Flour (T ha^{-1})	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**95.6 ± 7.7**
	1.0	**(1.02)**	BDL	BDL	BDL	BDL	BDL	BDL	**105 ± 12.0**
	2.0	**(1.03)**	BDL	BDL	BDL	BDL	BDL	BDL	**92.7 ± 19.2**
	5.0	**1.77 ± 0.14**	BDL	BDL	BDL	BDL	BDL	BDL	**86.2 ± 6.4**
	10.0	**2.37 ± 0.38**	BDL	BDL	BDL	BDL	BDL	BDL	**80.5 ± 8.0**
	20.0	**3.28 ± 0.29**	BDL	BDL	BDL	BDL	BDL	BDL	**82.7 ± 1.8**
Iceland Flour (T ha^{-1})	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**88.7 ± 6.0**
	1.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**86.6 ± 5.1**
	2.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**92.7 ± 7.8**
	5.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**87.9 ± 5.2**
	10.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**90.1 ± 5.1**
	20.0	0.00	BDL	BDL	BDL	BDL	BDL	BDL	**85.9 ± 2.6**
LOD		*0.80*	*0.50*	*0.50*	*1.40*	*11.2*	*3.10*	*1.40*	*50.1*

Table 5.8: Concentration of beneficial elements (ug g^{-1}) for the typical 'standard' soybean and the soybean glacial flour treatments from this crop growth experiment. Methodological limit of detection (LOD) also shown for all elements, values below the detection limit are indicated as BDL. Values in brackets are single replicate results only. Data is presented to 3 significant figures.

		Ca	Fe	K	Mg	Mn	Mo	P	S	Se	Sr	Zn
							(ug g^{-1})					
Typical Bean		1340	115	19500	3350	39.0	44.0	3750	2600	21.0	1.00	8.00
Control		1630 ± 90	175 ± 11	36900 ± 350	4800 ± 69	74.3 ± 3.5	35.5 ± 2.5	10800 ± 260	8270 ± 120	42.1 ± 8.5	(16.4)	**73.2 ± 5.2**
NPK fertiliser		1900 ± 120	167 ± 9	33900 ± 990	4230 ± 236	67.3 ± 5.1	44.4 ± 5.3	9070 ± 1460	7730 ± 330	BDL	(14.1)	**41.2 ± 8.9**
Himalaya Flour (T ha^{-1})	0.5	2160 ± 185	188 ± 7	36700 ± 363	4690 ± 85	75.0 ± 4.7	43.4 ± 2.2	9610 ± 350	8330 ± 160	BDL	BDL	**95.6 ± 7.7**
	1	2100 ± 156	195 ± 8	36100 ± 205	4700 ± 92	73.1 ± 10.5	44.1 ± 4.1	10100 ± 340	8840 ± 140	BDL	9.51 ± 6.9	**105 ± 12.0**
	2	1830 ± 162	171 ±12	34200 ± 220	4240 ± 88	62.4 ± 2.6	53.2 ± 3.8	9060 ± 150	7640 ± 160	(110)	(14.0)	**92.7 ± 19.2**
	5	2250 ± 230	191 ± 8	33500 ± 311	4250 ± 70	80.3 ± 5.4	57.6 ± 3.7	7520 ± 180	6890 ± 150	(115)	(16.1)	**86.2 ± 6.4**
	10	2190 ± 155	177 ± 14	34500 ± 325	4450 ± 102	78.7 ± 6.5	44.3 ± 3.9	7600 ± 210	8070 ± 160	(79.0)	17.2 ± 2.9	**80.5 ± 8.0**
	20	2120 ± 187	173 ± 16	35800 ± 169	4390 ± 98	88.9 ± 7.8	50.2 ± 4.6	8400 ± 200	7910 ± 140	(96.5, 208)	15.1 ± 1.9	**82.7 ± 1.8**
Iceland Flour (T ha^{-1})	0.5	2380 ± 164	186 ± 18	33300 ± 174	4270 ± 68	70.2 ± 6.5	59.9 ± 4.1	8390 ± 240	7740 ± 180	105 ± 13.9	15.4 ± 2.1	**88.7 ± 6.0**
	1	2880 ± 173	188 ± 22	30600 ± 168	4010 ± 95	75.4 ± 5.8	81.1 ± 4.2	7220 ± 180	7210 ± 150	125 ± 9.5	14.2 ± 0.2	**86.6 ± 5.1**
	2	3020 ± 196	209 ± 7	31400 ± 236	4180 ± 110	72.7 ± 5.9	84.0 ± 6.5	7110 ± 150	7390 ± 160	116 ± 14.7	19.2 ± 0.9	**92.7 ± 7.8**
	5	2170 ± 191	162 ± 9	31600 ± 302	4770 ± 126	75.8 ± 6.7	96.7 ± 5.9	7240 ± 220	7600 ± 190	130 ± 6.1	23.2 ± 5.2	**87.9 ± 5.2**
	10	2600 ± 200	161 ± 10	31900 ± 255	4350 ± 138	83.4 ± 8.8	104 ± 9.3	6700 ± 210	7200 ± 220	147 ± 7.0	18.2 ± 2.5	**90.1 ± 5.1**
	20	1930 ± 150	157 ± 28	33300 ± 368	4360 ± 117	87.5 ± 9.1	111 ± 8.4	7560 ± 190	7400 ± 140	133 ± 10.9	24.8 ± 3.9	**85.9 ± 2.6**
LOD		*560*	*50.8*	*78.8*	*57.3*	*315*	*45.5*	*260*	*882*	*0.70*	*7.3*	***50.1***

Table 5.9: Plant Toxic TE uptake (ug) for soybean glacial flour treatments from this crop growth experiment alongside maximum permissible limits and the typical 'standard' soybean concentrations. Values in bold are over permissible limits. Methodological limit of detection (LOD) also shown for all elements, values below the detection limit are indicated as BDL. Values in brackets are single replicate results only. Data is presented to 3 significant figures.

		As	Cd	Co	Cr	Cu	Ni	Pb	Zn
					(ug g^{-1})				
Indian Standard (2000)		1.1	1.50	-	20.0	30.0	1.50	2.50	50.0
FAO Codex (2013)		0.1	0.10	-	-	40.0	-	0.10	60.0
EU Standards (2012)		0.15	0.20	1.6	-	-	-	0.30	-
Standard Bean		0.01	0.01	0.00	0.01	0.00	0.00	0.00	8.00
Control		BDL	BDL	BDL	BDL	BDL	BDL	BDL	**35.1 ± 0.9**
NPK fertiliser		BDL	BDL	BDL	BDL	BDL	BDL	BDL	**86.2 ± 11.4**
Himalaya Flour (T ha^{-1})	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**62.3 ± 7.7**
	1.0	**(0.735)**	BDL	BDL	BDL	BDL	BDL	BDL	**88.4 ± 18.4**
	2.0	**(1.02)**	BDL	BDL	BDL	BDL	BDL	BDL	**92.1 ± 17.6**
	5.0	**2.30 ± 0.22**	BDL	BDL	BDL	BDL	BDL	BDL	**112 ± 21.3**
	10.0	**3.67 ± 0.85**	BDL	BDL	BDL	BDL	BDL	BDL	**124 ± 19.5**
	20.0	**5.34 ± 0.62**	BDL	BDL	BDL	BDL	BDL	BDL	**135 ± 23.6**
Iceland Flour (T ha^{-1})	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**66.3 ± 15.2**
	1.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**78.3 ± 17.0**
	2.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**101 ± 12.7**
	5.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**113 ± 13.0**
	10.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	**146 ± 15.6**
	20.0	0.00	BDL	BDL	BDL	BDL	BDL	BDL	**168 ± 20.5**

Table 5.10: Uptake of beneficial elements (mg) for the typical ‘standard’ soybean and the soybean glacial flour treatments from this crop growth experiment. Methodological limit of detection (LOD) also shown for all elements, values below the detection limit are indicated as BDL. Values in brackets are single replicate results only. Data is presented to 3 significant figures. Error is the standard deviation.

		Ca	Fe	K	Mg	Mn	Mo	P	S	Se	Sr	Zn
							(mg^{1})					
Control		1.01 ± 0.38	0.110 ± 0.027	19.8 ± 5.6	2.56 ± 0.56	0.024± 0.013	0.0140 ± 0.0033	5.83 ± 2.14	2.82 ± 2.81	0.013 ± 0.009	(0.0051)	0.0587 ± 0.0311
NPK fertiliser		0.64 ± 0.77	0.150 ± 0.034	53.5 ± 15.6	1.94 ± 1.31	0.062 ± 0.018	0.0470 ± 0.0195	12.4 ± 1.8	8.31 ± 2.88	BDL	0.008 ± 0.001	0.0549 ± 0.0511
Himalaya Flour (T ha^{-1})	0.5	1.38 ± 0.71	0.117 ± 0.032	22.8 ± 4.3	2.91 ± 0.59	0.054 ± 0.001	(0.0274)	5.94 ± 1.41	5.75 ± 0.15	BDL	BDL	0.0597 ± 0.0172
	1	1.74 ± 0.32	0.164 ± 0.030	30.2 ± 3.8	3.94 ± 0.57	0.059 ± 0.004	(0.0318)	8.38 ± 0.80	7.05 ± 0.05	BDL	0.011 ± 0.001	0.0883 ± 0.0251
	2	1.82 ± 0.93	0.169 ± 0.026	36.3 ± 4.5	4.53 ± 0.92	0.056 ± 0.0008	0.0494 ± 0.0081	9.43 ± 1.86	7.30 ± 1.25	(0.059)	(0.016)	0.0973 ± 0.0120
	5	2.98 ± 0.64	0.247 ± 0.053	43.3 ± 7.1	5.48 ± 0.39	0.098 ± 0.0007	0.0747 ± 0.0073	9.73 ± 2.02	8.27 ± 1.04	(0.167)	(0.024)	0.112 ± 0.022
	10	3.43 ± 0.67	0.274 ± 0.030	53.6 ± 9.7	6.91 ± 1.83	0.122 ± 0.013	0.0689 ± 0.0173	11.8 ± 2.87	13.5 ± 3.35	0.256 ± 0.242	0.0233 ± 0.0051	0.124 ± 0.021
	20	3.45 ± 1.24	0.280 ± 0.036	58.5 ± 15.2	7.17 ± 2.0	0.135 ± 0.017	0.0711 ± 0.0105	13.7 ± 3.0	12.5 ± 0.97	(0.112, 0.349)	0.0248 ± 0.0122	0.135 ± 0.036
Iceland Flour (T ha^{-1})	0.5	1.74 ± 0.56	0.139 ± 0.038	29.8 ± 2.3	3.83 ± 0.39	0.053 ± 0.021	0.0436 ± 0.0131	7.47 ± 2.15	5.88 ± 2.63	0.0765 ± 0.0281	0.0105 ± 0.0021	0.0793 ± 0.004
	1	2.59 ± 0.54	0.169 ± 0.032	36.4 ± 3.9	4.77 ± 0.31	0.059 ± 0.027	0.0730 ± 0.0271	8.59 ± 0.72	6.49 ± 1.87	0.113 ± 0.029	0.0172 ± 0.0039	0.103 ± 0.017
	2	3.27 ± 0.92	0.225 ± 0.032	42.1 ± 9.8	5.59 ± 1.16	0.089 ± 0.014	0.0926 ± 0.0723	9.56 ± 2.45	8.01 ± 2.02	0.116 ± 0.028	0.0256 ± 0.0200	0.125 ± 0.049
	5	2.78 ± 0.21	0.209 ± 0.048	40.6 ± 5.9	6.17 ± 3.33	0.097 ± 0.014	0.124 ± 0.0413	9.31 ± 1.35	9.76 ± 2.04	0.167 ± 0.024	0.0232 ± 0.0043	0.113 ± 0.012
	10	4.13 ± 0.24	0.260 ± 0.058	51.5 ± 2.8	7.01 ± 0.81	0.141 ± 0.025	0.169 ± 0.0422	10.8 ± 1.2	11.6 ± 4.1	0.237 ± 0.037	0.0292 ± 0.0105	0.145 ± 0.028
	20	3.76 ± 0.38	0.307 ± 0.024	65.1 ± 5.9	8.51 ± 0.51	0.142 ± 0.035	0.217 ± 0.0724	14.8 ± 1.9	14.5 ± 1.4	0.267 ± 0.048	0.0292 ± 0.0105	0.168 ± 0.007

Group 1 (Ca, Mg, Sr and Zn) elements had higher total concentrations in the soybeans treated by glacial flour compared to the control and NPK treatment. Icelandic flour treated beans had a greater biomass than Himalayan flour treated beans, and therefore, greater macronutrient uptake than Himalayan flour treatments. The influence of soybean biomass did not impact Ca, Mg, Sr and Zn uptake, where for both glacial flours as biomass and application rate increased, so did elemental uptake (Figure 5.2B, D, F, H, Table 5.8, 5.10). However, where uptake needs were greater, the concentration of Group 1 elements in the soybeans either decreased (Mg, Zn) or showed no significant response (Ca, Sr) to increasing glacial flour application rate. For example, for every 1 T ha^{-1} increase in Icelandic and Himalayan glacial flour, the results of the linear regression indicate there was 0.10 mg g^{-1} reduction in soybean Mg respectively (Iceland $R^2 = 0.65$ $p < 0.05$, Himalaya $R^2 = 0.68$ $p < 0.05$) (Figure 5.2A, C, E, G, Table 5.8, 5.10). Total Zn concentration decreased by 0.08 mg g^{-1} per 1 T ha^{-1} of application for Icelandic flour, and 0.06 mg g^{-1} per 1 T ha^{-1} for Himalayan flour (Iceland $R^2 = 0.97$, $p < 0.05$, Himalaya $R^2 = 0.96$, $p < 0.05$) (Figure G, Table 5.8, 5.10). For both glacial flours, Ca and Sr concentration was independent of the flour application rate (Figure 5.2A, E, Table 5.8, 5.10).

Group 2 elements, Fe, K, Mn, P and S, behaved similarly, in that concentrations were all within the range of the control and NPK treatment (Figure 5.3 A, C, E, G, I, Table 5.8), all treatments were enriched above the agricultural typical soybean. Uptake of Group 2 elements by the soybeans increased as glacial flour application rate and soybean biomass increased (Figure 5.3 B, D, F, H, J, 5.10) ($p < 0.05$).

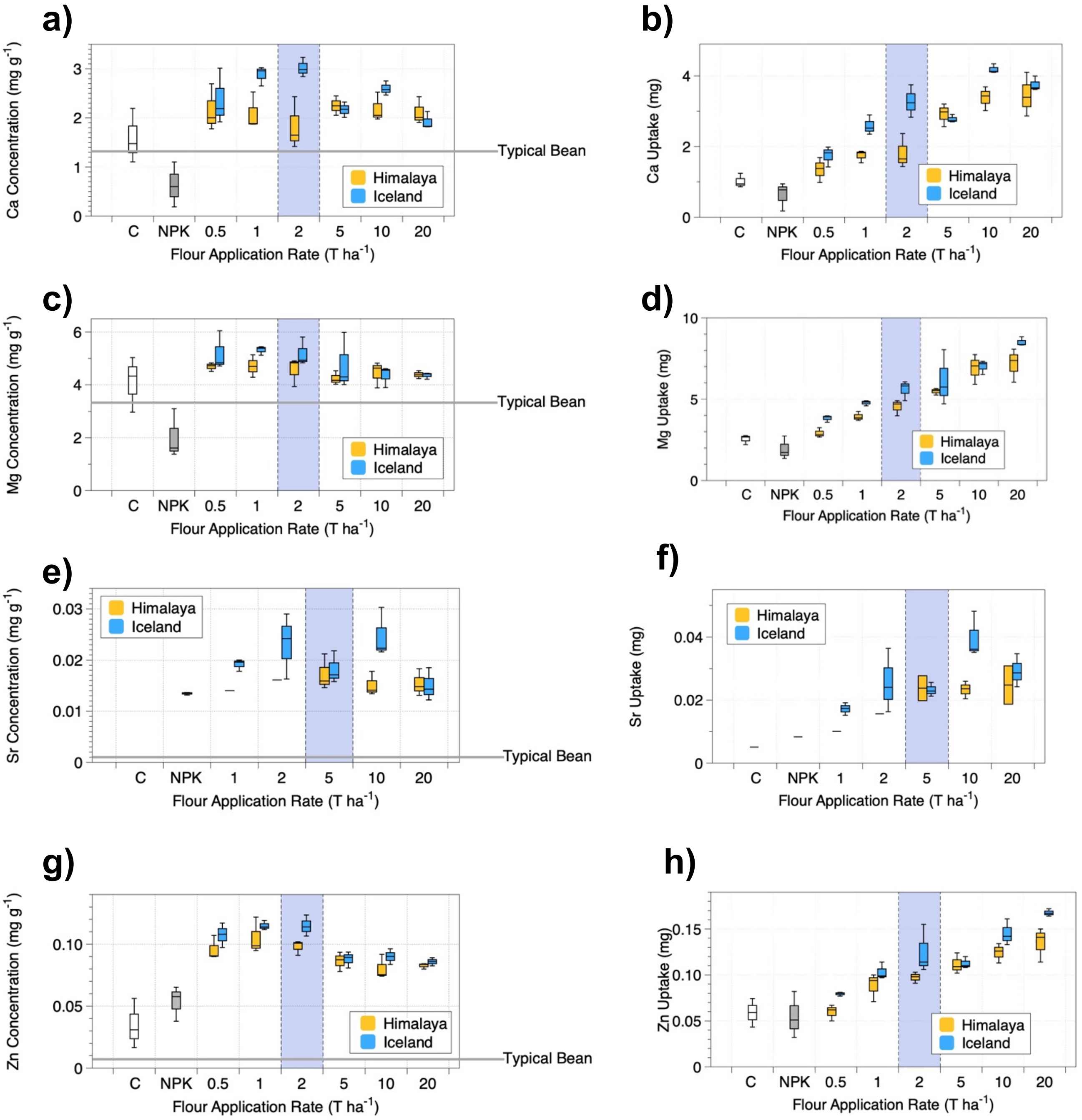

Figure 5.2: Group 1 elements Ca, Mg, Sr and Zn. Soybean seed element concentration (a) Ca, (c) Mg, (e) Sr, (g) Zn and uptake (b) Ca, (d) Mg, (f) Sr, (h) Zn. Showing in each figure, control (white), NPK fertiliser (grey) and glacial flour across all application rates (Himalaya and Icelandic flour, 0.5 T ha^{-1} – 20 T ha^{-1}). Grey 'typical soybean' line shows the standard typical agricultural bean concentration of each element.

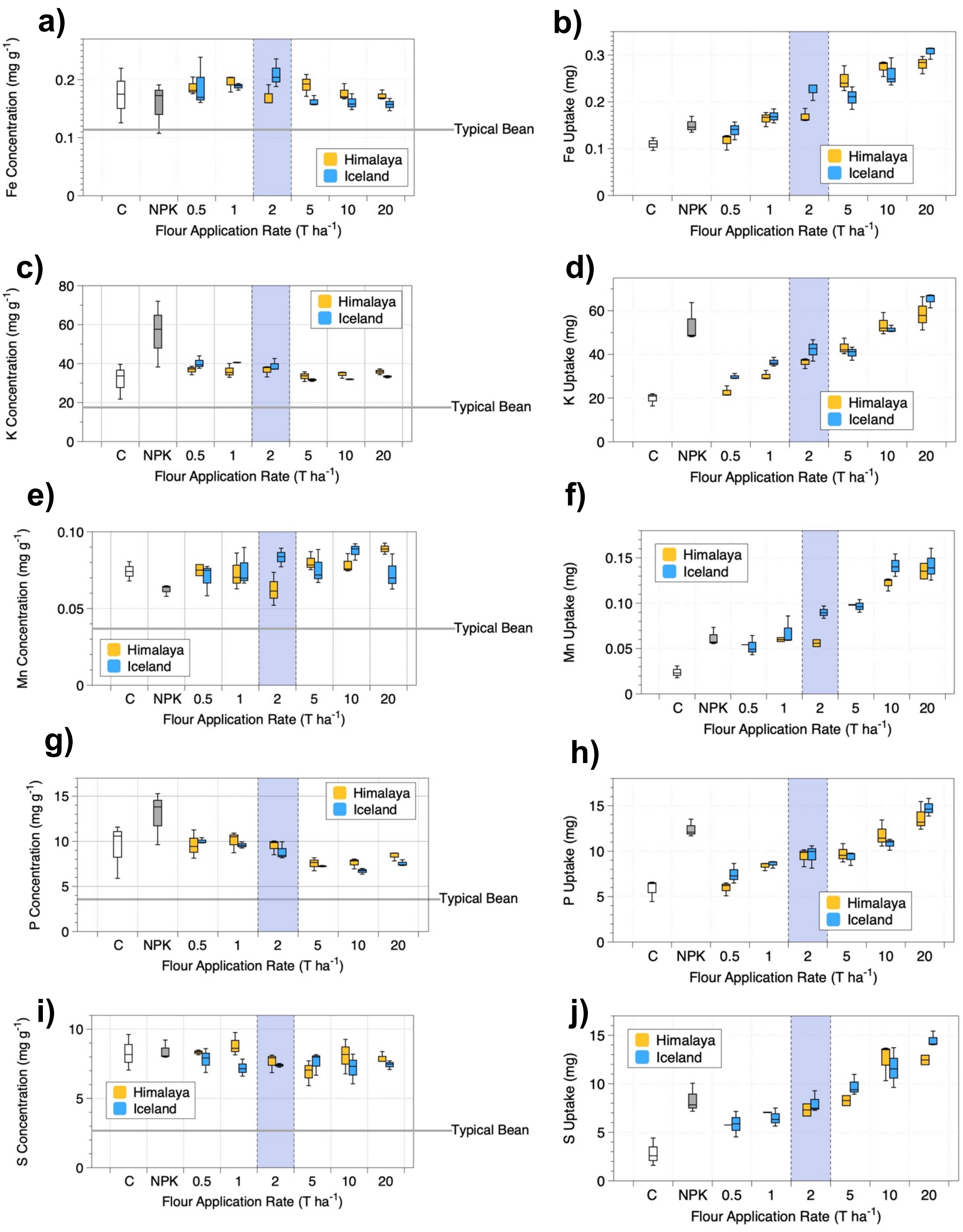

Figure 5.3: Group 2 elements Fe, K, Mn, P and S. Soybean seed element concentration (a) Fe, (c) K, (e) Mn, (g) P, (i) S and uptake (b) Fe, (d) K, (f) Mn, (h) P, (j) S. Showing in each figure, control (white), NPK fertiliser (grey) and glacial flour across all application rates (Himalaya and Icelandic flour, 0.5 T ha^{-1} – 20 T ha^{-1}). Grey 'typical soybean' line shows the standard typical agricultural bean concentration of each element.

This differs to Group 3 TE (As and Mo,), where concentration (Table 5.7, 5.8) and uptake (Table 5.9, 5.10) trends varied between the two glacial flours, but one flour displayed biofortification of bean concentration. Firstly, As was undetectable in all Icelandic flour treated soybeans, however, Total As concentration of Himalayan soybeans exhibited a strong positive correlation with glacial flour application rate. For every 1 T ha^{-1} of Himalayan flour, Total As concentration increased by 0.43 mg g^{-1} ($R^2 = 0.91$, $p < 0.05$) (Figure 5.4A, Table 5.7), this is further supported when calculating uptake, positive correlation with As uptake a Himalayan flour application (R2 = 0.97, $p < 0.05$) (Figure 5.4B, Table 5.9). Second, Mo in Himalayan flour showed no change in concentration compared to the Control / NPK (Figure 5.4C, Table 5.8) and no uptake application rate dependency (Figure 5.4D, Table 5.10, Mo $R^2 = 0.04$, $p > 0.10$). However, in Icelandic flour treated soybeans there was elevated Mo concentrations in line with increasing flour application rates (Table 5.8). For every 1 T ha^{-1} of Icelandic flour, Total Mo increased by 0.16 mg g^{-1} ($R^2 = 0.52$, $p < 0.05$), this equated to a very strong positive correlation with uptake and Icelandic flour application rate ($R^2 = 0.93$, $p < 0.05$) (Figure 5.4D, Table 5.10).

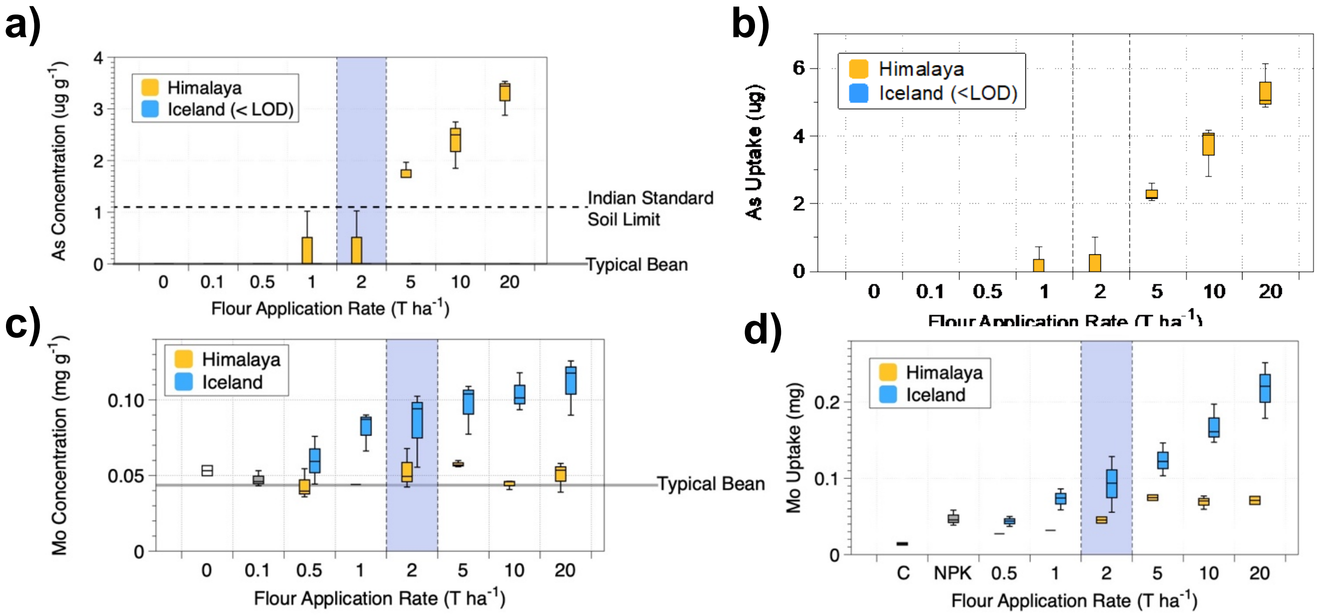

Figure 5.4: Group 3 elements As and Mo. Soybean seed element concentration (a) As, (c) Mo, and uptake (b) As, (d) Mo. Showing in each figure, control (white), NPK fertiliser (grey) and glacial flour across all application rates (Himalaya and Icelandic flour, 0.5 T ha^{-1} – 20 T ha^{-1}). Grey ‘typical soybean’ line shows the standard typical agricultural bean concentration of each element.

Finally, Group 4, Se, both glacial flours treatments at all doses achieved biofortification of Se soybean concentration at increasing doses; for every 1 T ha^{-1} of Himalayan and Icelandic flour, Total Se increased by 0.23 mg g^{-1} and 0.10 mg g^{-1}, respectively (Iceland $R^2 = 0.52$, $p < 0.05$, Himalaya $R^2 = 0.64$, $p < 0.05$). Se concentrations of the soybeans showed > 5 times enrichment at the lowest doses of glacial flours compared to the typical agricultural soybean (Figure 5.5 A, Table 5.8). The NPK treatment was < LOD, however the control treatment was slightly above the typical soybean concentration seen in agriculture (Figure 5.5A). The biofortification of the soybeans when combined with the crop biomass results in > 4 times larger uptake of Se (Figure 5.5 B, Table 5.10).

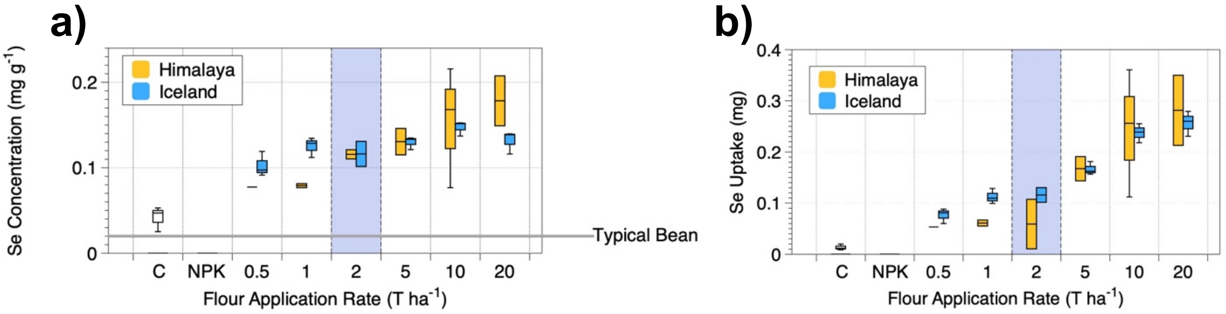

Figure 5.5: Group 4 elements Se. Soybean seed element concentration (a) and uptake (b). Showing in each figure, control (white), NPK fertiliser (grey) and glacial flour across all application rates (Himalaya and Icelandic flour, 0.5 T ha^{-1} – 20 T ha^{-1}). Grey 'typical soybean' line shows the standard typical agricultural bean concentration of each element.

5.4.3 Consumption of glacial flour enriched soybeans

Following Himalaya flour treatment, the soybean As concentration increased with flour dose and As consumption of a single portion of soybeans at the highest application rate of 20 T ha^{-1}, was 246 ± 2.5 ug (Total As, Table 5.11) which is significantly higher than the daily limit quoted by the jointly FAO / World Health Organisation of 100 ug Total As (Table 6) (Organization 2011). The consumption of one 75 g portion of soybeans grown in Icelandic and Himalaya flour across all measured flour application rates exceeded the daily intake limits for Mo and Se (Table 5.11).

Table 5.11: TE consumption (ug) for a 75 g portion of unshelled raw soybeans grown from this experiment, alongside the standard ‘typical’ soybean consumption. Values in brackets are single replicate results only. Values in bold exceeded the Daily Intake Reference Value (DIRV FAO Codex 2013), or the Daily intake limit (FAO / WHO 2017). Data is presented to 3 significant figures.

		As	Ca	Fe	K	Mg	Mn
		(ug)			*(mg)*		
Standard Bean		0.75	101	8.60	1470	251	2.93
Control		-	122 ± 10	13.1 ± 0.8	2770 ± 180	360 ± 56	5.57 ± 1.12
NPK fertiliser		-	142.5 ± 38	12.5 ± 3.6	2540 ± 364	317 ± 25	5.05 ± 1.33
Himalaya Flour (T ha^{-1})	0.5	-	162 ± 12	14.0 ± 1.2	2750 ± 200	351 ± 45	5.63 ± 1.78
	1	(76.5)	157 ± 16	14.7 ± 1.5	2710 ± 175	353 ± 78	5.48 ± 2.11
	2	(77.3)	138 ± 9	12.8 ± 2.0	2560 ± 143	318 ± 66	4.68 ± 1.36
	5	**133 ± 2**	169 ± 10	14.3 ± 0.9	2510 ± 188	318 ± 52	6.02 ± 1.85
	10	**177 ± 4**	164 ± 41	13.3 ± 1.4	2590 ± 203	334 ± 69	5.90 ± 1.79
	20	**246 ± 3**	159 ± 18	12.9 ± 1.3	2690 ± 247	329 ± 81	6.67 ± 2.06
Iceland Flour (T ha^{-1})	0.5	-	178 ± 16	14.2 ± 0.7	2500 ± 169	320 ± 35	5.27 ± 1.11
	1	-	216 ± 21	14.1 ± 1.1	2300 ± 206	300 ± 40	5.66 ± 1.95
	2	-	227 ± 15	15.7 ± 1.5	2350 ± 212	313 ± 50	5.46 ± 1.74
	5	-	163 ± 35	12.2 ± 0.8	2370 ± 195	358 ± 73	5.68 ± 1.42
	10	-	195 ± 10	12.1 ± 1.0	2390 ± 196	326 ± 47	6.25 ± 2.23
	20	-	145 ± 27	11.8 ± 1.2	2500 ± 223	327 ± 72	6.57 ± 1.89
DIRV FAO Codex (2013)			**1000**	**14**	**4700**	**320**	**3.0**
Daily intake limit (FAO / WHO 2017)		**100**	**2500**	**45**			**11.0**

Table 5.11 (Continued): TE consumption (ug or mg) for a 75 g portion of unshelled raw soybeans grown from this experiment, alongside the standard 'typical' soybean consumption. Values in bold exceeded the Daily Intake Reference Value (DIRV FAO Codex 2013), or the Daily intake limit (FAO / WHO 2017). Values in brackets are single replicate results only. There is no limit or RDA for elemental S. Data is presented to 3 significant figures.

		Mo	P	S	Se	Sr	Zn
				(mg)			
Standard Bean		**3.30**	281	195	**1.58**	0.04	0.60
Control		**3.99 ± 1.25**	811 ± 98	620 ± 155	**3.19 ± 0.95**	1.23 ± 0.21	5.16 ± 0.65
NPK fertiliser		**3.33 ± 1.56**	680 ± 111	580 ± 105	**-**	1.06 ± 0.56	3.09 ± 1.21
Himalaya Flour (T ha^{-1})	0.5	**(3.25)**	721 ± 103	625 ± 84	-	-	7.17 ± 0.84
	1	**(3.31)**	754 ± 95	663 ± 69	-	0.71 ± 0.18	7.85 ± 0.96
	2	**3.99 ± 0.65**	679 ± 62	573 ± 56	**(5.20)**	-	6.95 ± 1.02
	5	**4.32 ± 0.77**	564 ± 81	517 ± 87	**(5.29)**	-	6.46 ± 0.81
	10	**3.32 ± 0.93**	570 ± 78	605 ± 68	**(3.52)**	1.29 ± 0.54	6.04 ± 0.93
	20	**3.76 ± 1.01**	630 ± 55	593 ± 95	**(4.95, 16.3)**	1.13 ± 0.63	6.20 ± 0.65
Iceland Flour (T ha^{-1})	0.5	**4.49 ± 0.54**	629 ± 87	584 ± 89	**5.26 ± 0.82**	1.16 ± 0.68	6.65 ± 0.83
	1	**6.08 ± 1.02**	542 ± 65	539 ± 68	**9.38 ± 0.95**	1.07 ± 0.32	6.49 ± 0.98
	2	**6.30 ± 0.98**	533 ± 54	554 ± 66	**5.81 ± 1.05**	1.44 ± 0.55	6.95 ± 0.74
	5	**7.25 ± 1.03**	543 ± 60	570 ± 98	**9.73 ± 1.23**	1.74 ± 0.46	6.60 ± 1.07
	10	**7.82 ± 0.56**	503 ± 71	539 ± 103	**11.0 ± 1.18**	1.37 ± 0.62	6.76 ± 0.69
	20	**8.33 ± 1.17**	567 ± 84	557 ± 60	**9.86 ± 0.97**	1.86 ± 0.77	6.44 ± 0.55
DIRV FAO Codex (2013)		**0.045**	**700**		**0.06**	**0.6**	**6**
Daily intake limit (FAO / WHO 2017)		**2.0**	**4000**		**0.40**		**40**

All glacial flour treatments were below potentially toxic consumption daily limits (Daily intake limit (FAO / WHO 2017) for one 75g portion of soybeans Ca, K, P, S, Sr and Zn (Table 5.11). However, the consumption of a 75 g portion of soybeans treated in Himalaya and Icelandic flour resulted in beneficial consumption of elements to assist or meet the recommended daily intake values (DIRV FAO Codex 2013). Notably the consumption of glacial flour treated beans results in one portion meeting the Fe, Mg, Mn, P, Sr and Zn daily nutrient requirement for health (Table 5.11).

Multi-element pollution index (MPI) results showed that all treatments were well below the critical metal pollution level of 100 (Table 5.12, Figure 5.6). Both glacial flour treatments even at the minimum flour application rate (0.5 T ha^{-1}) were above the normal range for MPI in crops (7.3 – 13.5) but below the level considered "moderately enriched" in TEs (MPI 50) (Himalaya flour 20.5 ± 2.9, Iceland flour 27.5 ± 1.7) (Kumar, Shukla, et al. 2020). The MPI of Icelandic flour was independent of application rate ($R^2 = 0.02$), however the Himalayan flour treated soybeans where MPI was dependent on glacial flour application rate ($R^2 = 0.52$, $p < 0.05$).

The HRI was used to determine whether the consumption of glacial flour treated beans may have an impact on chronic dietary exposure to detectable TEs of concern (As, Fe, Mn, Mo, Se, Sr, Zn) (Singh et al. 2010) For glacial flour treated crops, the HRI for Cd, Cr, Fe, Mn, Mo, Ni, Pb, Se, Sr and Zn was < 1 (Table 5.13). However, two elements had HRI scores > 1. First, the HRI was >1 Mo across all glacial flour treated crops and doses (Table 7). Second, Himalayan flour treatments displayed HRI >1 for As over application rates > 2 T ha^{-1} (Table 5.13).

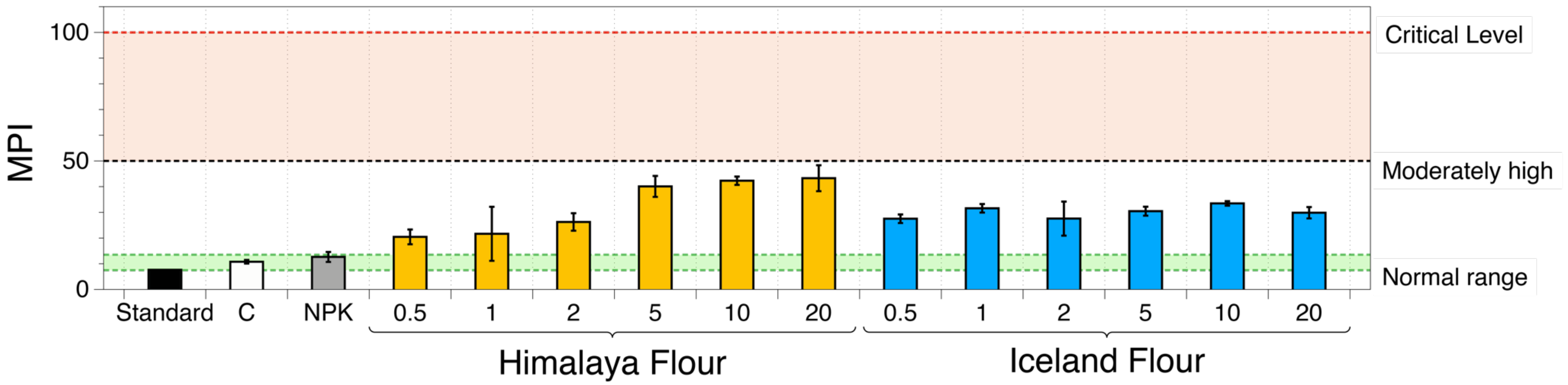

Figure 5.6: Metal Pollution Indexes, showing the standard soybean, control, NPK fertiliser and the two glacial flour treated crops across the range of application rates. The green range (7.3 – 13.5) indicates standard MPI scores for crops grown in India. MPI 50 = moderately high. MPI = 100 is critically polluted. Error bars represent the standard deviation of three replicate soybeans concentrations per treatment.

Table 5.12: Metal Pollution Index: Calculated values based on As, Fe, Mn, Mo, Se, Sr and Zn concentrations.

		MPI
Standard 'typical' soybean		7.65 ± 0.0
Control		10.8 ± 0.7
NPK fertiliser		12.7 ± 1.9
Himalaya Flour (T ha^{-1})	0.5	20.5 ± 2.9
	1	21.7 ± 10.5
	2	26.3 ± 3.4
	5	40.1 ± 4.1
	10	42.3 ± 1.6
	20	43.3 ± 5.0
Iceland Flour (T ha^{-1})	0.5	27.5 ± 1.7
	1	31.6 ± 1.7
	2	27.6 ± 6.6
	5	30.5 ± 1.7
	10	33.5 ± 0.9
	20	29.8 ± 2.2
Indian Agricultural Soils		7.3 – 13.5

Table 5.13: Health Reference Index scores for treatments. Shown to 2 significant figures, or 2 decimal places where appropriate.

		As	Cd	Cr	Fe	Mn	Mo	Ni	Pb	Se	Sr	Zn	Source
Control		0	0	0	0.091	0.02	0.00	0	0	0	0.00	0.01	This study
NPK		0	0	0	0.098	0.01	0.36	0	0	0.02	0.0007	0.01	
Himalaya flour (T ha^{-1})	0.5	0.95	0	0	0.099	0.01	0.26	0	0	0.08	0.0004	0.02	
	1	0.47	0	0	0.089	0.01	0.44	0	0	0.06	0.0008	0.02	
	2	2.46	0	0	0.099	0.02	0.48	0	0	0.07	0.0013	0.01	
	5	2.46	0	0	0.099	0.02	0.48	0	0	0.07	0.0013	0.01	
	10	3.29	0	0	0.092	0.02	0.37	0	0	0.13	0.0012	0.01	
	20	4.56	0	0	0.090	0.02	0.42	0	0	0.10	0.0012	0.01	
Iceland flour (T ha^{-1})	0.5	0	0	0	0.099	0.01	0.50	0	0	0.09	0.0011	0.02	
	1	0	0	0	0.098	0.02	0.68	0	0	0.10	0.0015	0.02	
	2	0	0	0	0.109	0.02	0.70	0	0	0.06	0.0018	0.02	
	5	0	0	0	0.085	0.02	0.80	0	0	0.11	0.0014	0.01	
	10	0	0	0	0.084	0.02	0.87	0	0	0.12	0.0019	0.01	
	20	0	0	0	0.082	0.02	0.93	0	0	0.11	0.0012	0.01	
Standard typical soybean		0	0	0	0.060	0.01	0.33	0	0	0.02	0.0004	0.00	
India													
Phaseolus vulgaris (French bean)		-	4.58	0.001	-	-	-	0.87	2.16	-	-	0.001	Chopra (2015)
Cabbage		-	10.16	5.47	-	-	-	0.83	1.68	-	-	0.00	Singh (2010)
Rice		-	6.87	4.32	-	-	-	7.98	31.59	-	-	1.52	

5.5 Discussion

5.5.1 Mineral weathering controls on element bio-accumulation

The TE composition of soybeans treated with Iceland and the Himalayan glacial flour indicates dominant weathering reactions that are ubiquitous in all lithogenic environments and well-studied in the subglacial domain (Wadham et al. 2010b; Tranter et al. 2002). Two key reactions that seem to determine TE enrichment in the soybean are carbonate and sulphide weathering, which are discussed below.

5.5.1.1 Carbonate weathering

The first driver of soybean TE enrichment appears to be associated with the weathering of Ca and Mg minerals, as elucidated from the enrichment of Total Ca and Total Mg in the soybeans and the concentration in both glacial flours. The order of magnitude higher Ca and Mg in Iceland flour than Himalayan flour is likely due to the presence of plagioclase feldspars and pyroxene minerals in basalts (Dessert et al. 2003). The retention and availability of cationic macronutrients (e.g. Ca, Mg, K) is dependent on the cation exchange capacity (CEC) of the soil (Chapman 1965). In this crop investigation, perlite, which comprises of 90 %vol of our artificial soil matrix, manufacturers indicate it has a very low CEC (< 1.5 meq 100 g^{-1}) and the compost (10 %vol) had a much higher CEC (~ 130 meq 100 g^{-1}) (Bunt 1988). The resulting CEC is much lower than agricultural field soils, when taking bulk soil density into account (artificial soil matrix 0.11 g cm^3, field soil 1.3 g cm^3). The CEC in the pot for field soil would equate to 191.1 meq pot^{-1} compared to our artificial soil matrix of 11.1 meq pot^{-1} (Biernbaum 1992). This relatively low CEC, combined with the soybean and associated rhizobia microbiota releasing organic acids and CO_2, may have driven the pH towards more acidic values throughout the course of the experiment (Drever 1994). However, the addition of glacial flour likely elevated the CEC due to its high mineral content, both acting as a pH buffer within the treatment pots and a source of nutrients.

The chemical dissolution of minor carbonate inclusions in basalt rich Icelandic flour-treated soybeans was likely a more readily available source of plant required macro and micronutrients compared to a lower carbonate-bearing rock type of Himalayan gneiss metamorphic-sedimentary bedrock (Jacobson et al. 2015). Thus, we observed the enrichment of TE commonly sourced from carbonate weathering in the soy beans e.g. Zn and Sr (Palmer and Edmond 1989), further supporting carbonate weathering as a driver for TE enrichment (Table 5.8). The chemical weathering of Group 1 elements (Ca, Mg, Sr and Zn) indicates their source for soybean trace element enrichment (Figure 5.2). Zn is most commonly found as zinc carbonate ($ZnCO_3$), known as calamine or smithsonite, and is generally a secondary mineral derived from the alteration of the primary zinc sulphide (ZnS), sphalerite, in oxidised geological zones (Wedepohl 1995). Sr is also found in high concentrations in carbonate minerals, whereby Sr^{2+} substitutes for Ca^{2+} and is therefore common in limestone, dolostones and evaporites (Wedepohl 1995). All soybean treatments in our experiments, including the control and NPK, were enriched in Total-Zn compared to the typical soybean in agriculture, this enrichment of Zn could be due to the potential availability of Zn in the perlite component of the artificial soil matrix, as evidenced by prior pot growth experiments where Zn becomes bound to ferric oxides (Fe_2O_3) (Table 5.1) (Silber et al. 2012).

This differs to the enrichment of Sr, whereby glacial flour treated soybeans were enriched in Sr well above standard soybeans, control and NPK treatments. Soybeans are not known to hyper-accumulate or bioconcentrate Zn, rather the uptake of Zn is tightly regulated by the availability of S (Balafrej et al. 2020). Successful Zn enrichment following glacial flour treatment may, therefore, be because of the addition of S, which was present in both glacial flours (Table 5.4). This is supported by recent work showing that simultaneous S and Zn application results enhanced Zn uptake and enrichment in soybeans (Zou et al. 2014). Importantly, glacial flour treated soybeans enriched in Ca and Zn have the potential to a be beneficial for human diets. Although the soybeans are enriched in Ca above the control and agricultural typical standard bean, they only meet a maximum of 22.7 ± 1.5 % and 13.8 ± 0.9 % of the daily recommended intake value (1000 mg) in 2 T ha^{-1} $^{\text{Icelandic}}$ flour and Himalaya treated soils respectively, as determined by the FAO Codex (2013) (Table 5.11). However, the Icelandic treated beans are significantly above the 12.2 ± 1.0 % and 10.1 % of the Ca daily intake requirement. In regions facing severe Ca malnutrition, biofortifying crops with Ca is a potential method to improve human dietary Ca consumption (White and Broadley 2009) (Table 5.11). Consumption of 1 portion (75 g) of soybeans grown in Himalaya and Icelandic flour at the lowest dose (0.5 T ha^{-1}) meets (120 ± 14 % and 116 ± 14 % respectively) the recommended dietary intake of Zn (6mg) as indicated by the FAO Codex (2013) (Sowa et al. 2014). Therefore, this study suggests that the enrichment of elements sourced from chemical weathering of trace carbonate minerals following glacial flour application may provide a sustainable strategy to biofortify soybeans to improve human health.

Soil-rock weathering environments can enhance the solubility of carbonate minerals and reduce the solubility of primary silicate minerals (Drever 1994; Sherlock, Lawrence, and Poulin 1995). In our study, TE extractions on the soybeans showed there was a lack of TE associated with silicate weathering, which would typically enrich the soybeans in some elements. For example Al, Co, Cr and Ni, which are higher abundance in silicate minerals than carbonate minerals (Rudnick and Gao 2014), were undetectable in the soybean crop despite a presence in both glacial flours (Table 5.5, 5.7).

5.5.1.2 Sulphide weathering

The second driver behind enhanced TE in glacial flour treated soybean crops is the weathering of sulphide minerals, for example, pyrite (FeS_2) which is the most abundant metal sulphide associated with the Earths crust and is mobilised by glacial physical and chemical weathering (Craig, Vokes, and Solberg 1998). TE commonly associated with sulphide minerals include Group 2, 3 and 4 elements; As, Cu, Fe, Mo, Pb, Se, and Zn (Taylor 1964; Wedepohl 1995). Both glacial flours contained S, Himalaya flour (0.026 ± 0.003 %) was within the normal range for continental crust (0.026 %) and granitic bedrocks (0.027 %) (Table 5.4) (Taylor 1964). However, Iceland was higher (0.066 ± 0.009 %), likely due to precipitation following S release from volcanic activity in the subglacial Katla volcano, lying beneath Sólheimajökull glacier (Table 5.4) (Wynn et al. 2015).

Group 2 elements, S and Fe were enriched in all treatments compared to the agricultural standard soybean concentration, likely due to Fe (from perlite and glacial flour) and S (from sulphates in the compost and flour) in the pots (Figure 5.1, Table 5.6). One reason for the lack of dose response for Fe and S enrichment may be that Fe and S were not limited in the soybean investigation. Alternatively, Fe and S are both key macronutrients involved in plant-rhizobia biological N-fixation and plant metabolism and are therefore are less likely to be assimilated into plant vacuole stores, but allocated to tissues to meet demand (Trivedi, Hemantaranjan, and Pandey 2011). However, three key TE commonly associated with sulphide rocks (As, Mo, Se) were all significantly enriched in glacial flour treated soybeans, and not in controls/chemical treated pots. The enrichment of the soybeans with TE commonly associated with sulphide rocks, indicates that sulphide oxidation weathering of glacial flour during or before the experiments took place and acted as a control on TE enrichment of soybeans (Figure 5.1A, B).

Group 3 and 4 elements, As, Mo and Se are strongly chalcophile elements ubiquitous within sulphide minerals of the upper crust (Kiseeva, Fonseca, and Smythe 2017). Glacial flour-treated soybeans were enriched in these chalcophile elements, however the level of enrichment differed between the two glacial flour sources. As is a non-essential plant element and is generally absorbed in either of the predominant inorganic forms, arsenate (As^{V}) or arsenite (As^{III}) that enter through P channels and aqua(glycerol)porins in root cells where it can become toxic for crops and bioaccumulate in humans, causing toxic arsenicism (Finnegan and Chen 2012). There was no As enrichment in soybeans above the control, NPK or any Icelandic flour treatments. However, we infer that Himalayan rocks including As-rich sulphide minerals were oxidised either in the flour during storage or in the pots, releasing As into the pot soil solutions, which suggests potential detrimental impacts for both the crop and human health (Perkins and Mason 2015).

Contrastingly, Mo and Se can be beneficial micronutrients for human diets if consumed at the recommended levels (Table 5.8). Mo is biologically inactive but important for successful legume growth, via its incorporation into a co-factor in enzymes such as nitrate reductase and sulphate oxidase (Ishizuka 1982). Despite the importance of Mo for plants, it is a relatively scarce element in soils and Mo-containing soil treatments have been proposed as a potential mechanism to boost legume yields [93]. Evidence in our investigation suggests that Icelandic flour may also be a beneficial source of geogenic Mo. Se can also be unavailable in the soil, with most regions of the world have soils that are Se-deficient and consequent human Se deficiency that increases the risk of cancer (Sors, Ellis, and Salt 2005). Recent work has attempted to biofortify crops with Se through geogenic soil treatments; research that is further supported by the evidence of Se enrichment from low dose glacial flour treatments in our study (< 2 T ha^{-1}) (Winkel et al. 2015). Overall, the enrichment of soybeans in Se and Mo indicates that glacial flour has the potential to act as a novel source of TEs, biofortifying soybeans for a more nutritious human diet. However, the As enrichment highlights a need to geologically screen soil treatments prior to inclusion in agricultural lands.

5.5.2 Beneficial or toxic treatment?

TE enrichment of glacial flour-treated soybeans suggests that glacial flour has potential as a pertinent mechanism to drive bioaccumulation of TE in soybean crops, specifically As, Fe, Mn, Mo, Se, Sr and Zn. The MPI of our control treatment (10.8 ± 0.7) showed that the artificial soil matrix was within the range of typical Indian agricultural soils (7.3 – 13.5) (Table 5.12) (Singh et al. 2010). Although presumed to be relatively inert, the perlite component of the soil matrix contained Fe and Zn (Table 5.1). However, glacial flour treatments enriched the pot in Fe and Zn, even the lowest application rate (0.5 T ha^{-1}) of both glacial flours resulted in a doubling of the MPI compared to the control treatment MPI (Table 5.12). TE that were enriched by Icelandic flour (Fe, Mn, Mo, Se, Sr and Zn) are beneficial for humans when consumed within recommended ranges and pose no multi-element toxicity concern. However, the MPI results suggest that multi-element toxicity is a potential risk for high application rate Himalayan flour treated beans (Figure 5.6, Table 5.12). At 20 T ha^{-1} the MPI of Himalayan flour treated beans (43.3 ± 5.0) was below globally concerning levels (50) (Zhang et al. 2014; Singh et al. 2010; Kumar, Shukla, et al. 2020). The dose dependent increase in MPI in Himalayan flour treated soybeans is likely due to the dominant increase in As, highlighting that crops grown on Himalayan flour rich soils may pose a multi-element toxicity risk to consumers.

Consumption of Icelandic glacial flour treated soybeans poses no chronic risk to health (HRI < 1 for all elements and application rates), including potentially toxic TE, As and Se (Yang et al. 1989). Although Icelandic soybeans had HRI < 1 for Mo, at the highest dose rate of 20 T ha^{-1} the Mo HRI was 0.93, this is likely due to the soybean species capacity to translocate Mo to their cotyledon when in the pod-filling stage of growth (Ishizuka 1982) (Table 5.12, 5.13). Soybean species are known to have a high quantity of Mo compared to other crops. It is unlikely that this level of Mo would be consumed across the entire human diet of crops grown in glacial flour treated soils (Davies 1956; Bambara and Ndakidemi 2010). The evidence from MPI and HRIs calculated from this investigation suggests that Icelandic flour can be used as a strategy to biofortify soybeans with beneficial TE for human diets even at low doses (< 2 T ha^{-1}) for two reasons. First, it may act as a suitable soil treatment to enhance micronutrients without causing detrimental toxic impacts. Icelandic flour could be used within an organic rich soil treatment, such as compost 'bokashi' mix, as a sustainable replacement for crushed rock or bone meal, acting as a multi-element soil enricher (Inckel et al. 2005). These soil treatments are commonly practiced in many low-input farming communities in mountainous regions and with fortunate geology, the inclusion of glacial flour could provide a low-cost method to enrich micronutrient status of agricultural soils (van Straaten 2006a; Beerling et al. 2018b; Altieri 2000). Second, the success of Icelandic flour shows that expansion of agricultural lands into deglaciating soils of similar geology, may be suitable for growing crops. However, we have only tested application rates up to 20 T ha^{-1} within an artificial soil matrix, further study investigating TE enrichment of crops within natural deglaciated environments is necessary to determine potential risks.

Exposure to As from crops grown on As-rich soils on a daily basis can cause acute and chronic adverse health effects, including cancer (Nriagu et al. 2007). Soil As can be taken up by all crops except those that are genetically modified to be As-resistant and likely expensive for use in low-input agriculture (Garg and Singla 2011). The results from this investigation highlight that crops grown on Himalaya flour-treated soil or expanding agriculture have a strong potential to cause chronic impacts upon human health from As toxicity. This may present a concerning development for future agriculture in the Himalaya region, with newly deglaciated glacial flour rich soils, or soils which are prone to glacial meltwater flooding and sediment deposition, particularly for the rural communities residing in the region reliant on low-input subsistence farming (Kumar, Kumar Singh, et al. 2020). Mountain communities downstream of Himalayas are a known hotspot for As toxic groundwaters, however the source of As from Himalayan glaciers has not been fully investigated until this study (van Geen et al. 2019).

5.6 Conclusion

We present the first dataset investigating the TE enrichment of soybeans grown in a glacial flour-amended nutrient depleted soil matrix. The controlled pot experiments were designed to determine if glacial flour acted as a source of macro/micronutrients and TEs in soybeans. The enrichment of beneficial TEs (Mg, Ca, Fe, Mn, Mo, Se, Sr and Zn) in the soybean crop were predominantly sourced from carbonate and sulphide weathering associated with chemical dissolution of glacial flours. Icelandic glacial flour was most beneficial for human diets, acting as a suitable source of beneficial macro and micronutrients in otherwise TE depleted-soils; potentially helping to provide a solution to ongoing mineral micronutrient malnutrition (e.g., Fe, Zn). However, the use of certain glacial flours, such those sourced from Himalayan bedrocks, in agriculture also has the potential to promote the bioaccumulation of trace elements such as As at toxic levels. This is concerning and points towards an urgent need to geochemically screen glacial flour, to determine potential toxicity in crop lands prior to expansion onto newly deglaciated land or following glacial flooding events. Nonetheless, our results indicate that where geology is suitable, low application rates of glacial flour have the potential be incorporated into current compost / soil amelioration treatments as a sustainable source of fertile elements whilst biofortifying crops with beneficial micronutrients e.g. Zn, Sr. Future work must look at whether TE are similarly enhanced in multiple crop cycles, or whether over time, silicate weathering increases and enhances alternative TEs such as Al, K, Cr, Ni, Si.

Chapter 6.
Concluding Discussion

The primary aim of this thesis was to fully evaluate the nutrient and elemental concentrations associated with glacial flour, and to determine its potential via crop growth experiments as a potential soil fertility solution. The former focussed upon the supply of beneficial macronutrients (P, K, Ca and Mg), micronutrients (Fe, Mn, Zn) and potentially toxic trace elements (As, Cd, Co, Cr, Cu, Pb, Sr, Se) from contrasting glacial flours, because of their influence upon potential crop yields and human nutrition. The experimental evaluation of glacial flour as a sustainable soil fertility treatment reflects the need for solutions to the projected global food security crisis, considering future climate warming, soil degradation and poor human diets. It intersects with the urgent need for sustainable, low-input farming methods for application by often resource-poor mountain communities. This final chapter summarizes the key findings of the thesis and highlights the implications for potential agroecological application of glacial flour within agriculture. It concludes with an overview of research gaps and suggestions for future studies.

6.1 Summary of main findings

6.1.1 Glacial flour as a significant source of nutrients of trace elements

The objective of this research was to identify how the nutrient content (macro and micronutrients), and speciation of glacial flour varies globally, evaluating the importance of bedrock. The aim of this research was to identify how the nutrient (P, K, Ca, Mg, S) and trace element (As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Pb, Se, Sr, Zn) content of diverse glacial flours varies globally, evaluating the importance of bedrock as a control, to assess its potential use as an agricultural soil amendment. This was achieved through a series of sequential and total elemental extractions upon a range of glacial flours from different bedrock types, with subsequent application of principal component analysis (PCA) to assess variation between different glacial flours and the potential geological drivers. This is the first comprehensive analysis to date of the elemental composition of glacial flours in understudied mountain glaciers. The results demonstrate that glacial flour elemental composition is a product of subglacial bedrock type and can contain an array of nutrients and trace elements which may be beneficial (P, K, Ca, Mg, S, Fe, Zn) for agriculture. However, the data also indicated that glacial flours from certain bedrocks may contain toxic trace elements (As, Cd, Co, Cr, Cu, Pb, Se, Sr and Zn) which may be detrimental to plant and human health. A summary of the conclusions of this chapter are as follows:

Hypothesis 1a: Nutrient content and speciation is determined by bedrock geology and mineralogy

Variation in glacial flour total and elemental concentrations showed close grouping via PCA analysis between glaciers with similar bedrock components in agreement with Hypothesis 1a. The elemental concentration of glacial flours sourced from igneous bedrock, Leverett, Kiattut Sermiat and Steffen glacier, showed low nutrient (P, K, Fe) content compared other glaciers studied. The glacial flours derived from glaciers with igneous-mafic basalts Falljökull and Sólheimajökull were the richest in all nutrients, with high P, K and Fe in the labile fraction. This is likely due to the basalt being rich in minerals such as plagioclase feldspars, pyroxenes and olivine. Metamorphic-Sedimentary bedrock glaciers, Arolla, Bara Shigri, Pastoruri and Shallap were high in P and K, however they all contain sedimentary rock components, which were particularly high in toxic trace elements linked to sulphides compared to other glaciers. Chotta Shigri and Tirich Mir, composed of mixed igneous-metamorphic-sedimentary bedrock were rich in P and K, whilst the TE content tended to shift in the PCA towards the dominant bedrock constituent of the three major rock types. Chotta Shigri was higher in sulphide components so sat within the metamorphic-sedimentary group. Whilst Tirich Mir was central to all three groups. Glacial flours composed of volcanic bedrocks had the highest proportion of beneficial micronutrients.

Hypothesis 1b: Glacial flour contains beneficial nutrients for crushed rock agriculture

Chemical extractions of important nutrients for plant growth in a diverse range of glacial flours showed elevated levels of nutrients comparable to those mechanically-crushed rocks studied in the literature, confirming Hypothesis 1b. Glacial flours with beneficial plant macronutrients (P, K, Ca, Mg, S) will likely chemically weather in soils due to their fine grain size and likely high reactivity. However, the results also showed that all glacial flours contained some trace elements at levels that may be beneficial as micronutrients (Fe, Se, Zn). Micronutrient deficient soils are difficult to remediate and have significant consequences for human health (Black 2003). This represents the first assessment of any crushed rock material as a source of micronutrients.

Hypothesis 1c: Glacial flour contains toxic trace elements with potential to be mobilised in soils

Results presented in Chapter 3 validated Hypothesis 1c, showing that all glacial flours contained toxic trace elements. Following glacial flour total element extractions, Chapter 3 showed that potentially toxic trace elements could exceed safe regulatory limits, for example As in Chotta Shigri glacial flour. These potentially toxic trace elements likely reflect the source bedrock concentrations, for example Chhota Shigri has sedimentary bands of shale. Whether or not these potentially toxic species attains harmful levels in soils and crops will depend upon a complex array of interacting factors, including glacial flour concentrations in soils and local soil chemistry (e.g., redox potential, acidity, organic matter content), making it important consider the impact of glacial flour application in a holistic manner.

6.1.2 Glacier to grain: glacial flour as a soil treatment for mountainous regions

The research reported in Chapter 4 addresses Objective 2 from Chapter 1 of this thesis, to perform an exploratory novel crop growth investigation to assess the effect glacial flour as upon the yield, health and nutritional value of leguminous crops. Objective 2 was addressed by an experimental pot-scale crop trials in which glacial flour was added in variable quantities to a low-nutrient soil matrix, simultaneously evaluating the impact on crop yields of the soybean (*Glycine max* var. Black Jet), plant health and dietary nutrition. This is the first investigation into the response of leguminous crops to glacial flour treatment within a controlled glasshouse environment using a low nutrient soil matrix (Sukstorf, Bennike, and Elberling 2020). Crop growth experiments compared the addition of two glacial flours from contrasting geological catchments: igneous-mafic basalt rock from Iceland; and granitic-gneiss (with minor sedimentary bands) from the Northwest Hindu Kush Himalaya, India. Himalaya and Icelandic glacial flour at an application rate of 2 T ha^{-1}, significantly enhanced crop yields by 85 % and 135 % respectively and improved plant health by 13.1 % and 14.9 % respectively. The Icelandic flour treatment grew the most nutritious crops in comparison to Himalayan flour, due to its higher concentration in beneficial nutrients and low toxic trace element concentration. However, the Himalayan soybeans were enriched in As. The results indicate that glacial flour derived from carefully selected geological terrains may serve as a potential soil improved in impoverished soils.

Hypothesis 2a: Glacial flour acts as a source of macro and micronutrients enhancing crop yields

There was a direct association between glacial flour application rates and crop yields, in agreement with Hypothesis 2a. The weathering of glacial flour within the experiment pots likely provided essential plant nutrients and micro-nutrients for crop growth. Glacial flours from both the Himalayas and Iceland improved yields by 85 % and 135 % at an application rate of 2 T ha^{-1}, however Iceland flour had a greater response (50 %). The importance of both bedrock mineralogy and particle size was highlighted since they are the complimentary drivers of crop yield gains in glacial flour experimental treatments. Importantly, glacial flour was as shown to be as successful in improving crop yield as low-rate chemical (NPK) fertilisers. This is believed to reflect the supply of micronutrients via glacial flour, which were minimal in chemical fertiliser treatments.

Hypothesis 2b: Glacial flour improves plant health and legume-rhizobia relationship

Results presented in Chapter 4 allow confirmation of Hypothesis 2b. Plant health (inferred from photosynthesis measurements), nodule counts, and crop yields displayed a close association with glacial flour application rate. Photosynthetic stress was lower in Himalaya and Iceland glacial flour treated soybeans compared to control (13.1 % and 14.9 % lower respectively) and chemical NPK fertiliser treatments (7.0 % and 5.4 % respectively). High nodule counts in soybeans treated with glacial flour (Himalaya 105 ± 24 and Iceland 150 ± 38) compared to the control (28.3 ± 15.2) and NPK fertiliser (51.8 ± 15.3) also indicated that the glacial flour improved the legume-rhizobia symbiotic nitrogen fixation relationship. The success of glacial flour over both the control and chemical fertiliser treatments is believed to reflect improved legume-rhizobia relationships due to the presence of micronutrients provided by the glacial flour. The data presented in Chapter 4 demonstrates the holistic positive impact glacial flour has upon legumes and suggests a potential wider use within agriculture.

Hypothesis 2c: Glacial flour has potential to enrich crops with beneficial nutrients for human diets

The results from Chapter 4 are in partial agreement with Hypothesis 2c. Soybeans treated with both Himalayan and Icelandic flour were enriched in beneficial micronutrients, showing a clear association between glacial flour application rate and enrichment factors. The enrichment of glacial flour-treated soybeans in micronutrients was above that measured in both the control and chemical fertiliser treatments. These results add weight to the potential for glacial flour within agriculture, suggesting that biofortification of the crop in micro-nutrients found in glacial flour can occur. However, the study also showed that Himalayan glacial flour enriched soybeans in the potentially toxic trace element, arsenic, which is concerning for both glacial flour application and/or the expansion of agriculture in mountain environments onto glacial soils. The results presented in Chapter 4 indicate that the future use of glacial flour within agriculture has potential, but that geochemical screening is necessary prior to use to avoid transfer of toxic trace elements from the flour to the crop.

6.1.3 Toxin or treat? Glacial flour as a source of beneficial and toxic trace elements for crops

The research presented in Chapter 5 was designed to answer Objective 3 outlined within Chapter 1, to evaluate the toxic bioaccumulation and beneficial biofortification of trace elements in glacial flour treated legumes. Chapter 5 advanced further from Chapter 4, by evaluating in greater depth the potential for the bioaccumulation of beneficial nutrients (‘biofortification’) or potentially toxic elements in crops grown on a glacial flour-influenced soil via the same glasshouse experiments in Chapter 4. This might include soils in high mountain regions, in addition to soils amended with glacial flour to improve soil fertility. Parallel chemical extractions of total elements from both glacial flours and the soybean crop represents the first comprehensive glass house of trace element mobilisation from soil to crops in crushed rock-amended soils. The results demonstrate that there are considerable differences between the trace element concentrations of the two different glacial flour treated soybeans, Iceland treated beans were not toxic in any elements, but beneficially enriched Zn to achieve 120 ± 14 % of the recommended dietary allowance. However, although Himalayan flour treated beans did beneficially enrich Zn to achieve 116 ± 14 % of the recommended dietary allowance, Himalayan flour soybeans displayed toxic levels of As. As enrichment was strongly dose dependent, at 20 T ha^{-1} was 2.5 times the WHO safe limit for consumption (246 ± 3 ug compared to 100 ug). This analysis indicates that the application of glacial flour has the potential to modify trace element concentrations in both soils and crops when applied within an agricultural context, creating the potential for both negative and positive impacts, depending on bedrock geology.

Hypothesis 3a: Glacial flour has the potential to enrich soybeans in macronutrients and trace elements

Evidence presented in Chapter 5 is concordant with Hypothesis 3a. However, this hypothesis is only true for certain elements, the behaviour of which could be separated into three groups. Group 1 elements; calcium, magnesium, and zinc, showed clear enrichment following glacial flour treatment above that observed in control and chemical fertiliser-treated pots. This suggests that the elements were provided by the weathering of glacial flour within the pot, and then transferred to the plant. Group 2 elements, namely iron, manganese, potassium, phosphorous and sulphur were not enriched above the control and chemical fertiliser treatment. This likely reflects the demand for these elements for plant growth and the fact that soybeans are not known to hyperaccumulate these elements (Liu 1997). Group 3 elements (arsenic, molybdenum, and selenium) displayed an enriched concentration in the glacial-flour treated crops compared with control and chemical fertiliser treatment, with each element showing unique patterns of enrichment behaviour, which also differed between the glacial flours.

Hypothesis 3b: The level of TE enrichment in the crop is dependent on glacial flour application rate

The results in Chapter 5 are in limited agreement with Hypothesis 3b; not all elemental concentrations in the soybeans displayed a direct positive association with glacial flour application rate. In the crops that had greater biomass because of glacial flour fertilisation, the soybeans had higher demands for nutrients and thus although larger uptakes of TE, the concentration showed little trend or decreased, this was applicable to Ca, Mg, Zn and Sr. The relationship between the total element concentration in glacial flour and the total element concentration of the soybeans across different glacial flour application rates was highly variable. In brief, different groups of elements displayed contrasting patterns of behaviour. The concentrations of Group 1 and 2 elements in the soybean crop were relatively insensitive to glacial flour application rate, while the concentration of Group 3 trace elements in the crop showed significant flour application rate dependency. However, the nature of the relationship between enrichment and flour application varied between different glacial flour treatments.

Hypothesis 3c: Bedrock source of glacial flour regulates crop element concentration through chemical weathering in experimental soils

In consensus with Hypothesis 3c the two contrasting glacial flours showed different element concentration and uptake patterns within the soybeans. Results showed that trace elements hosted in Iceland flour (basalt) and Himalayan flour (gneiss) were enriched to variable degrees in the soybean crop. This was most evident for Group 3 elements, where molybdenum and arsenic enrichment in the crop were unique to Iceland and Himalaya flour treatment respectively. It is likely that these differences in crop element enrichment reflected the mineral composition of the flour because of the bedrock geology. Specifically, the relative importance of silicate, carbonate, and sulphide dissolution in the experimental soils, likely impacted the different liberation of trace elements from the applied glacial flour.

Hypothesis 3d: Glacial flour application does not pose a risk to human health via either acute or chronic toxicity

Toxicity indexes performed on element extraction data from Icelandic treated soybeans corroborate Hypothesis 3d and suggested potential as a novel soil treatment for inclusion with low-input farming strategies. However, the toxicity assessment on the equivalent data from Himalaya treated soybeans does not support Hypothesis 3c and the employed toxicity indexes highlight concern for chronic health due to arsenic and multiple-element toxicity if the glacial flours were applied at application rate > 20 T ha^{-1}. The real-world impact of toxic arsenic from Himalayan rivers is well documented (van Geen et al. 2019), however, few studies have geochemically linked glacial flour as a source of arsenic to crops (Kumar, Kumar Singh, et al. 2020).

6.2 Main conclusions

1. **Glacial flour has potential as a novel sustainable soil fertility treatment within agriculture**

Although there is a significant body of research into the use of crushed rock as an agricultural soil fertility treatment, which has recently been revived due to its potential as a carbon sequestration strategy, there have been few studies assessing alternative sustainable low-cost sources of crushed rock (Mohammed et al. 2014; Manning and Theodoro 2020; Manning 2010; Bakken et al. 2000; Hensel 1894a; Bolland and Baker 2000a; van Straaten

2006a; Blanc-Betes et al. 2020; Beerling et al. 2018a; Sukstorf, Bennike, and Elberling 2020). The research presented in this PhD provides the first evidence that glacial flour from mountain glaciers has potential as a soil fertility treatment. All three complementary research chapters effectively build the case for glacial flour as a soil amendment.

The assessment of the nutrient and trace element content of diverse glacial flours presented in Chapter 3 indicates that glacial flour contains similar concentrations of P and K to those reported in past crushed rock research, where the latter have demonstrated successful crop yield gains (Priyono and Gilkes 2008b; Mohammed et al. 2014; Kelland et al. 2020). Complementary data from the crop growth investigation detailed in Chapter 4 and 5 suggest that the application of two contrasting glacial flour sources, Himalaya (gneiss) and Iceland (basalt), supplies nutrients and trace elements to soils, improving plant health, legume-rhizobia symbiosis, and nutrition. This is the first time that glacial flour from mountain glaciers sourced from proglacial landscapes in Iceland and the Himalayas have demonstrated to have a positive impact on crop growth. First, results indicate that some glacial flours, such as basaltic Icelandic flour may have strong potential as a soil amendment treatment. Even at low doses, Icelandic flour was successful in increasing crop yields, enhancing legume-rhizobia and enrichment in beneficial nutrients (e.g., Ca, Fe and Zn), suggesting its potential use within low-input farming agroecological strategies. Second, they indicate that some Himalayan glaciers may be suitable for agriculture due to high P and K, alongside plant essential trace elements Ca, Mg, Fe and S, but require geochemical screening prior to use to ensure that no harmful elements (As) have the potential to bio-accumulate in the crop, or farmers select crops that are resistant heavy metal bioaccumulation. Third, it highlights that deglaciating soils have potential to be rich geochemical reservoirs, with potential to provide fertile soils for farming in high latitude / altitude regions or potentially toxic landscapes unsuitable for agriculture.

2. Glacial flour can contain toxic elements that have the potential to bioaccumulate in crops and be harmful for human consumption.

One of the significant outcomes to this research via data presented across all three Chapters (Chapters 3 – 5) was the confirmation that glacial flour is not only a source of nutrients but can also be a source of toxicity. Data presented in Chapter 3 illustrated how different glacial flours can contain varied concentrations of toxic elements with some glaciers having less than the limit of detection and others having dangerous levels of toxicity due to bedrock components – particularly sulphide sedimentary bedrocks, seen in Shallap, Pastoruri, Bara Shigri, Chhota

Shigri and Arolla glacial flour (elements of concern; As, Cd, Co, Cr, Cu, Fe, Mn, Pb, Se, Sr, Zn). Chhota Shigri flour was then used in Chapter 4 to assess the potential for glacial flour as a leguminous crop soil fertility treatment, although Chhota Shigri flour increased crop yields (85 % compared to the control) and plant health (13.1 % compared to the control), the soybeans were enriched in As which was strongly correlated with glacial flour application rate ($R^2 = 0.97$, $p < 0.05$), this was further investigated in Chapter 5 where it was determined that one portion (75 g) of 20 T ha^{-1} Himalaya flour treated soybeans would result in consuming 2.5 times the permissible daily limit of Total-As. The research reported in Chapter 5 confirms that arsenic from Himalaya glacial flour has the potential to bioaccumulate in crops. The results from this body of work corroborate prior thinking that high groundwater, crop and river arsenic concentrations as seen in downstream Himalayan communities are potentially due to from glacial flour export (van Geen et al. 2019; Thakur et al. 2010; Paikaray 2012; Kumar, Singh, et al. 2020).

3. Bedrock lithology determines nutrient and trace element concentrations

Secondly, this study confirmed that bedrock lithology was the key determinant of glacial flour elemental composition. Past research into the biogeochemistry of glacial particulates has focused predominantly on large ice sheets such as Greenland, or glaciers in the Alps (Hawkings et al. 2015a; Hawkings, Skidmore, Wadham, Priscu, Morton, Hatton, Gardner, Kohler, Stibal, Bagshaw, et al. 2020; Hawkings et al. 2016; Cowton et al. 2012; Tranter et al. 2002). The data presented in Chapter 3 of this thesis builds on the pre-existing research, and includes lesser studied mountain glaciers, such as Bara Shigri, Tirich Mir in the Himalayas and Shallap and Pastoruri in the Peruvian Andes. This is the largest study so far to document nutrient and trace element concentrations from multiple glaciers located within catchments of varied bedrock type. Data in Chapter 3 indicated that glacial flours generally fall into one of four categories based upon bedrock type and subsequent trace element extraction. Glaciers were either in Group 1, metamorphic-sedimentary (Arolla, Bara Shigri, Pastoruri, Shallap), Group 2, mixed bedrock (Chhota Shigri, Tirich Mir), Group 3 igneous-mafic (Falljökull, Sólheimajökull), or Group 4 igneous-metamorphic (Kiattut Sermiat, Leverett, Steffen). Groups tended to have similar nutrient bioavailability of phosphorous and total elemental concentrations. The igneous-mafic volcanic basalts such as Falljökull and Sólheimajökull glacier had the highest concentrations of P in more labile fractions, potentially acting as a good source of flour for crops. The nutrient data presented in this study has potential to contribute to existing knowledge of glacial sediment nutrient fluxes (Hodson, Mumford, and Lister 2004; Hawkings et al. 2016; Föllmi et al. 2009).

6.3 Implications

This study strengthens the idea that glaciers can act as fertile ‘sediment factories’, producing finely crushed rock particles with significant nutrient and trace element contents (Chapter 3). A notable finding of this research was that glacial flour has potential to be used as a soil fertility treatment (Chapter 4). Even at low application rates (< 1 T ha^{-1}), this study showed glacial flour has the potential to enhance crop nutritional value via biofortification. This is especially important for two prospective markets, firstly the organic farming movement of some high latitude regions with large economic purchasing power and secondly, the low-input resource poor farmers of high altitude mountain regions in the Global South (Manning 2010). Glacial flour fertilisation of soils has only previously been assessed using Greenlandic ancient granitic bedrock but showed limited potential. However the findings from this body of work suggest glacial flours from different bedrock terrains e.g. Icelandic basalts, may have greater potential (Sukstorf, Bennike, and Elberling 2020). The significant improvement observed in crop yield, plant health, legume symbiosis by experiments presented in Chapter 4 suggests that glacial flour has potential for further assessment as a soil amendment.

The data from this research also suggested that plants can access nutrients and trace elements from glacial flour. This has conflicting implications dependent upon the elements in question. Previous work into the bioavailability of glacial flour has focused on microorganisms and algae, this is the first study into trace element uptake of glacial flour treated plants (Williamson et al. 2021; Kohler et al. 2018; Bradley, Singarayer, and Anesio 2014). Data presented in Chapter 5 suggested that glacial flour containing beneficial elements, such as Fe, Zn, led to the growth of a more nutritious crop, therefore strengthening the potential of utilising glacial flour as a novel soil amendment strategy. However, the results in Chapter 5 also indicated that glacial flour containing higher concentrations of potentially toxic trace elements could result in a potentially toxic crop for human consumption if applied at high rates (> 5 Tha^{-1}). This has potentially serious consequences for communities residing downstream of glaciers capable of producing toxic glacial flours that could poison crops and cause long term health issues (van Geen et al. 2019; Kumar, Singh, et al. 2020). The potential impact of toxic elements from glacial flour to downstream communities requires further investigation. Future research should determine potential toxic element fluxes from mountain glaciers with significant downstream populations – Himalayas, Andes. Furthermore, future studies should determine toxic trace element speciation of dissolved and sediment fluxes for example As(III) is up to 10 times more toxic than As(V) due to high solubility (Ratnaike 2003)

This thesis provides evidence that glacial flour has potential to act as a novel, sustainable soil treatment strategy in line with the 2030 United Nations Sustainable Development Goals (Nations 2015). Glacial flour has the potential to act as a potential soil fertility treatment for crops, enriching crop yields, plant health, nitrogen fixation and nutritional value. Iceland flour acted as the geochemically 'ideal' glacial flour and was the most successful across all measured parameters. However, although Himalaya flour positively impacted crop yield, plant health and nitrogen fixation, the nutrition value of the soybean product was severely impacted by the toxic trace elements. Future work must assess whether glacial flour can be geochemically screened at low cost for use within sustainable low-input agriculture. However, the toxic elements that impacted the soybean crops from Himalaya treated soybeans highlight that future discussions regarding future changes to meltwater supply from glaciers includes consideration of water quality as well as water quantity. The importance of glacial flour nutrient and trace element supply should also be assessed in the context of deglaciation, as glacial sediment rich landscapes are impacted by warming climates and longer growth seasons this can give rise to rapid 'greening' growth of which trace element biogeochemical cycles are largely unknown (Myers-Smith et al. 2020; Heffernan 2013; Arndt et al. 2019). The main finding of this research is that glacial flour can act as a source of nutrients and trace elements to plants.

6.4 Limitations, knowledge gaps and future research

Despite this thesis achieving multiple significant findings, there are some limitations. Presented below are the limitations and remaining knowledge gaps, complemented by recommendations for future research.

- **Bioavailability of trace elements.** Although Chapters 3, 4 and 5 present data on the phase association of phosphorous in glacial flours, more research is needed to fully evaluate the potentially labile component of P in addition to that of trace elements. Furthermore, mineralogical data on glacial flours was lacking, making it challenging to infer relationships between mineralogy and nutrient/trace element availability in amended soils. It is likely that the uptake of trace elements by plants is controlled by the how tightly bound the trace element is to specific minerals, for example, elements bound to iron oxides may be more labile than carbonate minerals (Velbel 2009; Robert and Berthelin 1986; Lucas 2001; Drever 1994; Chigira and Oyama 2000). Furthermore, the roles of subglacial weathering and proglacial processing in transforming glacial flour particles is unknown, which may affect choices of where flour for agricultural application would best be sampled. Future research might employ sequential extraction studies of trace elements to determine speciation and improve understanding of bioavailability for plants.

- **Information on weathering mechanisms.** Despite data from the crop investigation indicating which weathering processes may dominate nutrient and trace element release from glacial flour, there was insufficient time to specifically evaluate chemical weathering processes in experimental investigations. It is likely that carbonate and sulphide mineral weathering were the presiding weathering mechanisms, resulting in the mobilisation of trace elements from soils to crops in this study. Future research needs to establish the weathering mechanisms of glacial flour within soil to fully understand nutrient and trace element release. This could be achieved by performing weathering experiments, firstly, investigating glacial flour weathering within a soil matrix only through pot microcosm experiments, measurements of gas fluxes, CO_2, N_2O and pore water dissolved nutrient content (e.g., N, P, C) would determine active weathering. The same measurements could be performed on a larger pot investigation including plants and a field study.

- **Issues of scale in glasshouse crop investigation.** There are five limitations to the findings of this glasshouse investigation. First, this study only assessed two glacial flours but data from Chapter 3 suggested that the bedrock beneath glaciers varies considerably. Second, this thesis focussed its evaluation of glacial flour application to a single leguminous crop species. Thus, it is unknown how glacial flour may act upon other species, such as wheat, vegetables, and fruit trees. Third, this study is limited by its understanding of glacial flour within real world soils since the glasshouse study employed an artificial soil matrix. Thus, conclusions cannot be drawn regarding real-world weathering and glacial flour fertility potential. The experiments in this study were performed in a controlled environment in small scale pots, and the impact of varied temperatures and water regimes upon plant resilience was not considered. Finally, conclusions the effect of seasonal crop cycles on glacial flour may influence mobilisation of nutrients and trace elements from glacial flour. The pot investigation performed in this study clearly highlights the multiple benefits glacial flour may have for agricultural soils. However, before recommendations surrounding glacial flour use are implemented field trials are necessary. Addressing the knowledge gaps outlined will improve our understanding of its potential and develop best practice recommendations for its use.

- **Impact of the source of glacial flour.** Our study is limited to knowledge surrounding the impact of freshly collected glacial flour from as close to the glacial river outflow ("portal") as possible. However, the most practical environment from which to sample glacial flours for agricultural use are places where glacial flour is deposited in reservoirs and estuarine harbours, and ordinarily is regularly dredged to avoid sedimentation issues. Evaluating the impact of aged glacial flours on potential nutrient release for crops would provide critical information regarding its potential impact within agriculture and for plant and human health. It would also allow for an assessment of potential sustainable sources of glacial flour for crops. Understanding the efficacy of glacial flour from these potential sources is likely to have significant implications in the development of glacial flour for agriculture.

- **The role of glacial flour weathering on downstream biogeochemical cycles.** Currently our knowledge of glacial flour nutrient and trace element supply to downstream ecosystems focuses on species that are key to marine productivity. Future studies need to be more extensive to ascertain the importance of trace elements to downstream ecosystems and to evaluate whether there are correlations with their supply and primary production in both marine and freshwater environments. One key research gap is the lack of knowledge surrounding nutrient and trace element cycles following glacial meltwater flooding events and subsequent glacial flour deposition on land. Mining and removal of Himalayan river sands for construction, is of growing concern and it is unknown whether these sediments are of glacial origin and if there are any impacts of their removal upon downstream ecosystems (Bendixen et al. 2019).

- **Economic costs of the use of glacial flour for agriculture.** This thesis has ma determined glacial flour nutrient and trace element content and investigated the potential of glacial flour as a soil amendment. This study has advanced understanding of the impact of glacial flour upon crop yield and plant health. However, future research into potential costs, such as transportation, labour and carbon costs are necessary to fully understand the sustainability of amending soils with glacial flour. It is essential to understand costs if glacial flour application to soils is to be implemented at scale.

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