MASTERARBEIT / MASTER'S THESIS

Titel der Masterarbeit / Title of the Master's Thesis

„What drives nutrient diffusion in soils?“

verfasst von / submitted by

Denisa Finta

angestrebter akademischer Grad / in partial fulfillment of the requirements for the degree of

Master of Science (MSc)

Wien, 2023/ Vienna, 2023

Studienkennzahl lt. Studienblatt / degree programme code as it appears on the student record sheet:	UA 066 299
Studienrichtung lt. Studienblatt / degree programme as it appears on the student record sheet:	Interdisziplinäres Masterstudium Environmental Sciences
Betreut von / Supervisor:	Univ.-Prof. Dr. Wolfgang Wanek

List of abbreviations

$\frac{dC_L}{dC}$ = solute sorption on the soil solid matrix

- R = sink

+ R = source

AEC = anion exchange capacity

c (equivalent to C_{eq}) = equilibrium concentration of the sorptive in solution (mol L^{-1})

CEC = cation exchange capacity

C_{eq} = concentration of the sorptive (mol L^{-1})

C_L = concentration in soil solution

D = diffusion coefficient or diffusivity in water (m^2 s^{-1})

D = diffusion constant

D_e (or D_s for soils) = diffusion coefficient in porous media (m2 s-1)

D_e = effective diffusion coefficient

D_L = diffusion coefficient in liquid

D_w = diffusion coefficient in aqueous solutions (m^2 s^{-1})

dx = path length (m)

$d\varphi$ = concentration difference (concentration gradient) (mol m^{-3})

EEA = microbial extracellular enzyme activity

FAA = free amino acids

f_L = impedance factor, related to the geometry and tortuosity of the soil pore network

ICP-MS = inductively coupled plasma mass spectrometry

J = diffusive flux (mol m^{-2} s^{-1})

K and n = constants for a given solute (K) and adsorbent (n), at a given temperature.

k_B = Boltzmann constant

K_d or K_f – Freundlich solid-water distribution coefficient = soil adsorption coefficient (L kg^{-1})

K_{oc} = organic carbon-normalized distribution coefficient

K_{ow} = octanol-water partition coefficient

m = mass of adsorbent (sorbent, soil)

MD = microdialysis

microCT = microtomography technique

n.a = not applicable

PFT = pedotransfer function

Q_{10} value = temperature sensitivity

R = radius of the sphere (molecule)

SOC = soil organic carbon

SOM = soil organic matter

SSA = specific surface area (m^2 g^{-1})

SSR = source-sink relations

T = absolute temperature

VWC = volumetric water content

x = mass of adsorbate (sorbate)

x/m (equivalent to Γ_{ads}) = equilibrium concentration of the sorbate (mol kg^{-1})

Γ_{ads} = concentration of the sorbate (mol kg^{-1})

δ = constrictivity (dimensionless)

ε_t = porosity available for transport (dimensionless)

θ_L = fraction of soil volume occupied by soil water, equivalent to volumetric water content (VWC), representing the cross-sectional area for diffusion

τ = tortuosity (dimensionless)

η = viscosity

List of Tables:

List of equations:

Abstract

Diffusion is considered to be the main transport mechanism of limiting nutrients like nitrogen and phosphorus in terrestrial systems. Diffusion is influenced by the interrelationship between chemical, biological and physical soil properties. Any change in these system properties can therefore influence other factors in contrasting ways and thereby affect diffusive fluxes. The main focus of this study was to acquire detailed information about the different biotic and abiotic controls affecting diffusive nutrient fluxes in soil as well as to deepen the understanding on the importance for plant nutrition. Studies based on microdialysis technology provided a substantial amount of available data to compile and assess controls regarding diffusive solute fluxes. As described by Fick`s law, the main drivers of diffusion are diffusivity, concentration gradient, and path length. Diffusivity is affected by physicochemical soil and solute properties affecting the mobility of solutes in soil solution. Solute concentration gradients are governed by biological activities including source-sink reactions and by abiotic ones affecting sorption/desorption. The path length is controlled by soil physical parameters such as porosity and soil water content. Overall further research should be conducted on solute diffusion in the field and more focus should be laid on the potential that microdialysis has to offer to accurately analyze nutrient availability in-situ and with minimal disturbances.

Kurzfassung

Die Diffusion gilt als der wichtigste Transportmechanismus für limitierende Nährstoffe wie Stickstoff und Phosphor in terrestrischen Systemen. Die Diffusion wird durch die Wechselbeziehung zwischen den chemischen, biologischen und physikalischen Bodeneigenschaften beeinflusst. Jede Veränderung dieser Systemeigenschaften kann daher andere Faktoren auf gegensätzliche Weise beeinflussen und sich somit auf die Diffusionsflüsse auswirken. Das Hauptaugenmerk dieser Studie lag auf der Gewinnung detaillierter Informationen über die verschiedenen biotischen und abiotischen Faktoren, die die diffusiven Nährstoffflüsse im Boden beeinflussen, sowie auf der Vertiefung des Verständnisses der Bedeutung für die Pflanzenernährung. Studien auf der Grundlage der Mikrodialysetechnik lieferten eine beträchtliche Menge an verfügbaren Daten zur Zusammenstellung und Bewertung von Kontrollen der diffusiven Stoffflüsse. Wie im Fick'schen Gesetz beschrieben, sind die Hauptfaktoren für die Diffusion die Diffusivität, der Konzentrationsgradient und die Weglänge. Die Diffusionsfähigkeit wird durch physikalisch-chemische Boden- und Lösungseigenschaften beeinflusst, die sich auf die Mobilität der gelösten Stoffe in der Bodenlösung auswirken. Die Konzentrationsgradienten der gelösten Stoffe werden durch biologische Aktivitäten, einschließlich Source-Sink-Reaktionen, und durch abiotische Aktivitäten, die die Sorption/Desorption beeinflussen, bestimmt. Die Pfadlänge wird durch bodenphysikalische Parameter wie Porosität und Bodenwassergehalt gesteuert. Insgesamt sollte die Diffusion von gelösten Stoffen im Feld weiter erforscht werden, und das Potenzial der Mikrodialyse zur genauen Analyse der Nährstoffverfügbarkeit in-situ und mit minimalen Störungen sollte stärker in den Vordergrund gerückt werden.

Table of Contents

1. Introduction

Plant nutrient acquisition is a complex process that is fundamentally controlled by the availability and continuous replenishment of nutrients to the root surface. Besides root interception, the two major mechanisms supplying nutrients to plant roots are mass flow and diffusion (Lambers et al., 2008; Tinker & Nye, 2000). Mass flow is driven by plant transpiration and by precipitation, causing water potential differences to trigger mass flow via plant transpiration or gravitational rainwater infiltration into soils. This results in the mass transport of water and nutrients from the soil to root surfaces. Diffusion, on the other hand, describes the movement of molecules through soil along a concentration gradient between root surfaces and the surrounding soil. The latter is driven by the root uptake of nutrients causing their depletion in the root vicinity relative to higher concentrations in bulk soils, without the net movement of water (Buckley et al., 2020). It is generally believed that diffusion is the main driver of the fluxes of limiting nutrients from soil to plant roots in nutrient-poor soils, while mass flow is of greater importance in nutrient-rich soils or for nutrients in lower demand than is supplied by soil, causing no concentration gradients between roots and the soil solution (Barber, 1995; Oyewole et al., 2014; Smethurst, 2000). Moreover, nutrient supply via diffusion becomes increasingly important when there is nutrient deficiency and the plant's nutrient demand cannot be met by mass flow (Comerford, 2005). Relative contributions of mass flow and diffusion to soil nutrient supply vary depending on the nutrient and soil physical, chemical and biological properties (Loladze, 2002; McGrath & Lobell, 2013; Van Vuuren et al., 1997). This further implies that transpiring plants may encounter a different composition of nutrients, compared to non-transpiring plants (Oyewole et al., 2014). Due to this complex interrelation of different soil factors, the relative contribution of diffusion and mass flow to plant nutrient supply is still a matter of controversy.

This short review aims to summarize the current knowledge of the factors controlling soil nutrient supply via diffusion in order to better understand the importance of soils supplying macro- and micronutrients to plant roots (and microbes) (Griffiths & York, 2020). The author is not aware of any current comprehensive review of the influence of different soil physical, chemical, and biological factors on the diffusion of nutrients in soil systems sustaining plant nutrient uptake. Despite the importance of diffusion for nutrient provisioning there have been little comparative studies across nutrients and different soil types, hindering real data synthesis and the development of predictive models. The majority

of the available studies focus only on a few environmental factors and on one nutrient or solute/ion but do not address the multitude of factors and their influence on nutrient diffusion processes. Towards this end, this review aims to synthesize existing knowledge on nutrient diffusion in soils, on the factors that control the diffusion of nutrients, as well as how biotic and abiotic factors are interconnected. A large part of the recent scientific progress in this area is based on microdialysis approaches which have gained momentum for the analysis of solute diffusion in soils, providing new data on this important process (Buckley et al., 2020).

2. Methodology

A detailed literature investigation was conducted on diffusive fluxes of nutrients in soils and the soil properties that directly or indirectly impact nutrient diffusion in soil systems. Literature research was conducted using multiple library databases such as Web of Science, ResearchGate, Google Scholar and Science Direct, searching for keywords such as "soil", "diffusion", "nutrient", solute", microdialysis", "availability", among others.

The conventional methods that involve sampling of nutrient fluxes include lysimeter applications and soil extractions (e.g. with strong salts). An alternative method to measure nutrient availability through diffusion fluxes in soil systems is through microdialysis technique. It is a microscale level, non-invasive technique with minimal disturbance to surroundings and real-time in situ measurements. It can be used both in a lab and on the field. ***Table 7*** offers a synthesis of the works published so far on the application of microdialysis across different compounds.

3. Drivers and controls of diffusion of solutes in soil

Diffusive fluxes of a nutrient (solute) are proportional to the concentration gradient and inversely related to the path length, modulated by the diffusivity of the solute, according to Fick's first law of diffusion.

Equation 1. Fick's first law of diffusion

$$J = -D\frac{d\varphi}{dx}$$, where

- J is the diffusive flux, in amount (moles) of substance per unit area per unit time. It indicates the amount of a substance that flows through a unit area during one unit of time (mol m^{-2} s^{-1}).

- D represents the diffusion coefficient or diffusivity in water (also: self-diffusion coefficient), in area per unit time ($m^2\ s^{-1}$). It is proportional to the squared velocity of the diffusing solute, which depends on temperature, the viscosity of the fluid, and the size of the solute.
- $d\varphi$ is the concentration difference (concentration gradient) in dilute solutions such as soil water, with the dimension of difference in the amount of substance per unit volume (mol m^{-3}).
- dx is the distance between two positions, the dimension of which is length (m).

Each of the parameters included in Equation 1 (diffusivity D, concentration gradient $d\varphi$, path length dx) is influenced by a complex interplay of soil physical, chemical and biological parameters. For example, diffusivity is affected by abiotic sorption of solutes to the soil matrix which in turn is influenced by *inter alia* temperature, solute concentration, molecular radius and charge. Solute concentration gradients in soil are controlled by source strength and supply which are mainly (but not only) affected by biological activities such as mineralization, enzymatic decomposition, and microbial turnover. The path length for diffusion, on the other hand, is largely controlled by soil physical parameters, e.g., soil porosity, pore size distribution, pore connectivity and water filled pore space.

Since soil physical, chemical and biological parameters are interlinked and influence each other, it is important to disentangle the controlling factors directly influencing solute diffusion in soils. The following chapters thus focus on the major controls of diffusivity, concentration gradient and path length.

3.1 Controls of diffusivity

In dilute aqueous solutions the diffusion coefficients D_w of most solutes are similar, at room temperature ranging between 0.6 and 2.0×10^{-9} $m^2\ s^{-1}$ for small molecules (***Table 1***). Large biomolecules diffuse more slowly, with proteins having D_w of 10^{-10} to 10^{-11} $m^2\ s^{-1}$. In porous media, however, the diffusion coefficient D_e (or D_s for soils) is reduced compared to pure water, due to volumetric restrictions to the water-filled pore space and due to solute-matrix interactions, causing the sorption and deceleration of molecular diffusion of solutes. Depending on (i) a solutes' molecular size, the charge density and charge type (anions versus cations), and its hydrophobicity, and (ii) the physicochemical properties of the soil medium through which the solute is diffusing, the diffusion coefficients in soils are 10^1- to 10^6-fold

lower compared to those in water (***Table 2***). Below the effects of sorption processes on diffusive fluxes in soils are discussed. Inert solutes diffuse faster than metabolically active ones, small ones faster than large ones (proteins), and neutral metabolites (sugars) faster than ionized ones (amino acids, deprotonated organic acids; ***Table 1***).

Table 1. **Diffusion coefficients of solutes in water (D_w) and in soils (D_e, D_s). Units: $m^2\ s^{-1}$**
cited from (Table of Diffusion coefficients, 2020; Diffusion coefficients in water, n.d.)

Solute	**D_w** ($m^2\ s^{-1}$, 25 °C)	**D_s, D_e**	**Soil condition, reference**
OH^-	5.27×10^{-9}	n.a	25 °C, saturated
Cl^-	2.03×10^{-9}	$0.16\text{-}0.62 \times 10^{-9}$ $0.4\text{-}1.6 \times 10^{-10}$	saturated; unsaturated (Olesen et al., 1999)
Br^-	2.01×10^{-9}	n.a	(Barraclough & Tinker, 1982)
HCO_3^-	1.18×10^{-9}	n.a	(Annan, 2012)
NO_3^-	1.90×10^{-9}	$0.5\text{-}3.2 \times 10^{-10}$	(Barraclough & Tinker, 1981; Hill, 1984)
$H_2PO_4^-$	0.88×10^{-9}	n.a	
HPO_4^{2-}	0.76×10^{-9}	0.5×10^{-12}	(Bhadoria et al., 1991)
SO_4^{2-}	1.06×10^{-9}	3.6×10^{-10}	
H^+	9.31×10^{-9}	1×10^{-10}	Quartz sand
NH_4^+	1.97×10^{-9}	$0.2\text{-}1 \times 10^{-11}$	(Olesen et al., 1999)
Na^+	1.33×10^{-9}	n.a	
K^+	1.96×10^{-9}	3.31×10^{-10}	(Conkling & Blanchar, 1989)
Ca^{2+}	0.79×10^{-9}	1.24×10^{-10}	(Conkling & Blanchar, 1989)
Mg^{2+}	0.71×10^{-9}	1.08×10^{-10}	(Conkling & Blanchar, 1989)
Zn^{2+}	0.72×10^{-9}	1×10^{-12} to 10^{-15}	diff. VWC and BD

Fe^{3+}	0.60 x 10^{-9}	2.2 x 10^{-10}	
Al^{3+}	0.56 x 10^{-9}	n.a	
Amino acids (Gly)	1.10 x 10^{-9}	1 x 10^{-11}	(Darrah, 1991b)
Amino acids (Gln)	0.76 x 10^{-9}	1 x 10^{-11}	
Sugars (Glc)	0.67 x 10^{-9}	(0.1 x 10^{-9})	(Darrah, 1991a; Dorodnikov et al., 2009)
Sugars (Sucr)	0.52 x 10^{-9}	n.a	
Organic acids	1.21 x 10^{-9} (Acetic acid)	n.a	(Darrah, 1991b)
	1.09 x 10^{-9} (Acetate)	1 x 10^{-11}	
	1.00 x 10^{-9} (Benzoic acid)	n.a	
	0.86 x 10^{-9} (Benzoate)	n.a	
Protein (lysozyme)	0.22 x 10^{-9} (14.4 kDa)	n.a	
Protein (GFP)	0.09 x 10^{-9} (27 kDa)	n.a	(Schavemaker et al., 2018)

3.1.1 Temperature, viscosity and molecular size

In principle diffusion rates and diffusion coefficients increase with temperature, and decrease with viscosity and molar mass (size, radius). This is given by the Stokes-Einstein relation, stating the following for a sphere of radius *R* immersed in a fluid,

Equation 2. Stokes-Einstein

$$D=\frac{k_B.T}{6\pi\eta R},$$

where *D* is the diffusion constant, k_B is the Boltzmann constant, *T* is the absolute temperature, η is the viscosity, and *R* is the radius of the sphere (molecule). In a microdialysis study conducted by Inselsbacher and Näsholm (2012b), they assessed the effect of temperature on diffusive fluxes of inorganic nitrogen (N) and organic N compounds in two distinct soil types. They demonstrated that temperature increases diffusive fluxes of soil N compounds,

with diffusive fluxes increasing by 2.4% per °C in water, following predictions from the Stokes-Einstein relation, but 2.6 to 6.6% per °C in an agricultural and a boreal forest soil. The larger stimulations of diffusive fluxes in soils were found, the smaller the compounds were in mass.

Finally, diffusive fluxes of individual amino acids were linearly and inversely proportional to their respective molecular weight in water (Inselsbacher & Näsholm, 2012b). From 6 to 22 °C the viscosity of water declined from 1.533 to 0.942 g m^{-1} s^{-1}, therefore markedly accelerating diffusive fluxes at higher temperatures. It has also been noted that diffusive fluxes increased from arctic to subtropical biomes. However, temperature does not only affect diffusion but also other underlying processes such as sorption, desorption, enzyme activity and biological uptake, with potentially different temperature sensitivities. This temperature sensitivity is also expressed as Q_{10} values, depicting the change in process rate with a temperature increase of 10 °C (***Table 2***). According to this analysis Q_{10} values of abiotic processes (1.0-2.0; diffusion, sorption, and desorption) were lower compared to biological processes (1.5-3.2; enzyme activities, uptake, respiration, growth), indicating lower temperature sensitivities of the former processes.

Table 2. **Temperature sensitivity (Q_{10} values) of various processes underlying nutrient diffusion in soils.**

Process	**Q_{10}**	**Temperature range, reference**
Diffusion of Cl^-	1.35	10-20 °C
	1.42	0-10 °C
Diffusion of amino acids	1.26-1.63	>6 °C (Inselsbacher and Näsholm, 2012b)
Diffusion of lysozyme	1.1	(Svanidze et al., 2012)
Sorption	1.0-1.2	(Conant et al., 2011)
Desorption	1.2-2.0	(Conant et al., 2011)
Extracellular enzymes	1.5-2.5	(Baldrian et al., 2013)
Intracellular mineralization	2.4	(Holland et al., 2000)
Microbial growth	2.1-3.2	(Zheng et al., 2019)
Facilitated passive uptake	1.5	(Agalakova et al., 1997)
Secondary active transport	2.5	(Agalakova et al., 1997)

Active transport	1.9-3.0	(DuPont, 1989)

3.1.2 Sorption processes and sorption coefficients

Sorption processes in this regard refer to a surface phenomenon, i.e. the (reversible) binding or adhesion of free solutes in soil solution onto the surface of soil particles, controlling solute availability for uptake by biota and for soil losses to surface waters and groundwater. This occurs through various mechanisms, including adsorption and precipitation reactions on particle surfaces, their contribution to sorption depending on the chemical nature of the solute. The mechanisms differ in terms of time kinetics, sorption strength and influencing factors relating to the nature of the solute (valence, hydrophobicity, electron configuration) and of the soil matrix (soil mineral and organic matter surface properties).

The most important **sorption mechanisms** are: ion-exchange, Ca^{2+} bridging, ligand exchange, precipitation, complexation, hydrophobic interactions, Van der Waals forces and H-bonding (Strawn, 2021). These can be classified as **outer sphere reactions** (e.g. ion exchange) and **inner sphere reactions** (e.g. ligand exchange). Outer sphere (ion-exchange) reactions are fast, caused by electrostatic attraction of opposite charges and characterized by relatively weak bonding energies between the charged solute and adsorbent. In inner sphere reactions solutes become part of the mineral surface, due to covalent bonding following ligand exchange, and adsorption/desorption show strong hysteretic behavior. Inner-sphere reactions can form (i) covalent-type bonds between metals or oxyanions (e.g. phosphate) and mineral edges with reactive O ligands or with phenolic/carboxylic groups of soil organic matter (SOM), or (ii) ionic-type bonds between dehydrated cations (K^+, NH_4^+) and permanently charged O atoms on basal planes of vermiculite and illite. Precipitation can occur onto any mineral surface, particularly involving oxyanions such as phosphate, and transition metals such as iron. Hydrophobic partitioning causes Van der Waals binding/interactions between hydrophobic organic chemicals (e.g. lipids, fatty acids, organic pollutants) with uncharged regions of SOM and kaolinite. Hydrogen bonding, Van der Waals and capillary forces also entrap solutes (through absorption) in microcavities in porous media and aggregates.

Sorption is described as the equilibrium between dissolved and sorbed states of a solute, which can be described by (quasi-)equilibrium reactions. Further, the adsorption of solutes is represented by **adsorption isotherms**, showing the amount of adsorbate (adsorbed

solute) on the adsorbent (sorbent, soil) as a function of its solution concentration at constant temperature, which is commonly normalized to the mass of the adsorbent. Different mathematical models were developed, the **Freundlich isotherm** and the **Langmuir isotherm** models being the most widely used ones. The Freundlich adsorption isotherm is an empirical relationship between the concentration of a solute adsorbed onto the surface of a solid and the concentration of the solute in the liquid phase:

Equation 3. Freundlich adsorption isotherm

$$\frac{x}{m} = K\, c^{1/n}, \text{ or}$$

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log c, \text{ with}$$

x = mass of adsorbate (sorbate)

m = mass of adsorbent (sorbent, soil)

(equivalent to Γ_{ads}) = equilibrium concentration of the sorbate, i.e. sorptive/solute sorbed onto soil (in mol kg^{-1})

c (equivalent to C_{eq}) = equilibrium concentration of the sorptive (free solute) in solution (in mol L^{-1})

K and n are constants for a given solute (K) and adsorbent (n), at a given temperature.

The sorption strength - and inversely proportional to this the mobility - of a solute in soil is related to the **distribution coefficient** or the **soil adsorption coefficient, K_d**, or the Freundlich solid-water distribution coefficient K_f, Γ_{ads} representing the concentration of the chemical in soil (mol kg^{-1}) divided by C_{eq} the concentration in water (mol L^{-1}) (therefore K_d in L kg^{-1}).

Equation 4. Soil adsorption coefficient

$$K_d = \frac{\Gamma_{ads}}{C_{eq}}$$

Values of K_d vary greatly because the organic matter content of soils is not considered in the equation, which is, however, important for the sorption of many organic compounds and transition metals, among others. Normalization of K_d to soil organic carbon (SOC) therefore gives the distribution coefficient as organic C-normalized distribution coefficient, K_{oc}.

Equation 5. Organic carbon-normalized distribution coefficient

$$K_{oc} = K_d \frac{100}{\%SOC}$$

During the last 40-50 years there have been multiple attempts to derive these distribution coefficients from the solutes' physicochemical properties. For example K_{oc} was frequently related to K_{ow}, the octanol-water partition coefficient, and water solubility (Briggs, 1981; Gawlik et al., 1997), or later derived from surface complexation or universal solvation models (Goldberg, 2014; Winget et al., 2000) and/or from quantitative structure-activity relationships based on quantum mechanical descriptors and machine learning (Doucette, 2003; Huuskonen, 2003).

At low concentrations the relationship between Γ_{ads} and C_{eq} is close to linear (with K_d as its slope), while at high external concentrations this relationship becomes non-linear, approaching a sorption plateau (maximum sorption capacity). Below are presented the soil adsorption coefficients of selected inorganic and organic chemical compounds (***Table 3***). This sorption capacity is strongly dependent on factors outlined below, i.e. texture, mineralogy, soil organic matter (SOM) content, and pH. Pedotransfer functions (PFTs) have been developed to estimate maximum sorption capacities of different soils based on more easily available or measurable quantities, e.g. for phosphate based on oxalate- and dithionite-extractable Fe/A-O contents or the prediction of cation exchange capacity (CEC) based on soil pH, texture, SOC and land use (Borggaard et al., 2004; Mishra et al., 2022; Scheinost & Schwertmann, 1995).

Table 3. **Soil adsorption coefficients (K_{oc}, or K_d, in L kg^{-1}) of selected inorganic and organic chemical compounds. Adsorption coefficients are presented as log10 values (with K_{OC} and K_d untransformed in brackets).**

Compound	**log K_{oc} (K_{oc})**	**log K_d (K_d)**	**Reference**
Barium	n.a	1.78 (60)	MINTEQ model
Arsenic (+3)	n.a	0.52 (3.3)	MINTEQ
Zinc	n.a	1.58 (38)	MINTEQ
Glucose	n.a	1.89 (77)	(Jagadamma et al., 2012)
Alanine	n.a	2.32 (207)	(Jagadamma et al., 2012)
Salicylic acid	n.a	1.80 (63)	(Jagadamma et al., 2012)
Sinapyl alcohol	n.a	0.88 (7.7)	(Jagadamma et al., 2012)

Oxalic acid	n.a	2.09 (1233)	(Jagadamma et al., 2012)
Acetone, C_3H_6O	-0.20 (0.6)	n.a	MINTEQ
Acetic acid, $C_2O_2H_4$	0.00 (1.0)	n.a	(Sabljić et al., 1995)
Ethanol, C_2H_6O	0.20 (1.6)	n.a	(Sabljić et al., 1995)
Benzoic acid, $C_7H_6O_2$	1.50 (31.6)	n.a	(Sabljić et al., 1995)
Benzoate	0.50 (3.2)	n.a	MINTEQ
Thiourea, CH_4N_2S	0.85 (7.1)	n.a	(Huuskonen, 2003)
Nicotine, $C_{10}H_{14}N_2$	2.01 (102)	n.a	(Huuskonen, 2003)
Naphthalene, $C_{10}H_8$	3.1 (1023)	n.a	(Winget et al., 2000)
Di-n-octyl phthalate, $C_{24}H_{38}O_4$	8.06 (1.14×10^8)	n.a	MINTEQ

3.1.3 Controls of sorption processes: texture, mineralogy, pH, CEC/AEC

Soil texture is expressed as the relative proportion of sand, silt, and clay in a given soil. Porosity varies depending on particle size and aggregation and is greater in clayey and organic soils than in sandy soils. A fine soil has smaller but more numerous pores than a coarse soil. Conversely, a coarse soil has larger particles than a fine soil, but it has less porosity, or overall pore space. Clays have predominantly small pores, and sands have large pores (Ball, 2001). Most soils are a mixture of sand, silt and clay particles, generating a mixture of different sized soil pores and a tighter soil particle packing. Therefore, texture has an influence on plant nutrient supply capacity, soil organic matter (SOM) storage, soil water drainage, and the soil's capacity to absorb and store nutrients (Eash et al., 2015). Delgado and Gómez (2016) pointed out that soil texture can predict the infiltration rate of a soil and is strongly related to its CEC. Fine-textured, clayey soils, have greater specific surface area (SSA), CEC, and nutrient-holding capacities as opposed to coarse-textured, sandy soils, as well as larger soil organic matter storage capacities due to the larger surface area of fine textured minerals (see ***Table 4***). With regards to diffusion, solute diffusion rates are expected to be higher in coarse-textured soils, due to their larger pore diameters, which permits rapid water and air movement (Eash et al., 2015).

Soil mineralogy, comprising clays, quartz, and other primary minerals, clay minerals and Fe/Al oxides, hydroxides and oxyhydroxides (in short "Fe/Al-O"), play a key role in

determining the solute sorption potential of soils and therefore exerts a prominent control on diffusive fluxes of solutes in soils. Clays and Fe/Al-O form through weathering processes. **Clay minerals** are hydrous aluminum phyllosilicates with variable contents of iron, alkali metals and alkaline earths. They can be categorized as 2:1 and 1:1 clay minerals, as they are built of tetrahedral silicate (SiO_4) sheets and octahedral hydroxide ($Al_2(OH)_6$) sheets. Clays of the 1:1 structure, e.g. kaolinite, consist of one tetrahedral sheet and one octahedral sheet, while 2:1 clays, such as vermiculite and montmorillonite, consist of an octahedral sheet sandwiched between two tetrahedral sheets (Kumari & Mohan, 2021). Important characteristics of clay minerals differentiating them include (1) their effective sorption capacity for nutrient cations and anions, and pollutants (Behroozi et al., 2021), (2) their water retention capacity and swelling properties (expandability), and (3) their negative permanent electric charge due to isomorphic substitution, which leads to their variable cation exchange capacity (Wang et al., 2017).

Table 4. **Selected clay minerals and their properties, including sandy to clayey soils. CEC…cation exchange capacity (meq (100 g)$^{-1}$, equivalent to cmol charge kg^{-1} soil dry weight for monovalent cations), SSA…specific surface area (m^2 g^{-1}). n.a. …not applicable**
(*Clay and Clay Minerals*, 2021)

Name	**Type**	**CEC** (pH 7)	**AEC**	**SSA** (N_2)	**Properties**
Sand	n.a.	<2	0	0.1-2	n.a
Organic matter	n.a.	250-450	n.a	560-800	Polyethyleneglycol adsorption instead of BET
Kaolinite	1:1	3-15	3-5	5-40	non-expandable
Halloysite	1:1	40-50	n.a	1100*	expandable
Chlorite	2:1:1	10-40	n.a	10-55	non-expandable, Mg/Fe-rich
Illite	2:1	10-40	1	10-100	non-expandable, K/Mg/Fe-rich
Vermiculite	2:1	100-150	1	760*	expandable, Mg/Fe-rich

Smectite	2:1	80-120	1	40-800	expandable, Na/K/Mg-rich
Montmorillonite (smectite group)	2:1	80-100	n.a	40-600	expandable, Na/K/Mg-rich

Clay mineralogy and soil porosity therefore have a strong predictive role for solute diffusion in soil systems. Diffusive fluxes are higher in vermiculite-rich as opposed to smectite-rich soils, due to the different swelling behavior of the clay minerals and differences in pore structures (Tertre et al., 2018). The **specific surface area (SSA)** is the combined surface area of all particles in a soil sample, given as $m^2\ g^{-1}$, and is measured as physical adsorption of N_2 or water, or the retention of ethylene glycol (or ethylene glycol monoethyl ether). The SSA measured by N_2 sorption varies very largely, from ~10 for sand to 100 for montmorillonite, and up to 650-800 $m^2\ g^{-1}$ for smectite group clays (Kumari & Mohan, 2021; Pennell, 2016). SSA increases linearly with clay percentage of soils and is unrelated to soil organic matter content, whereas CEC scales strongly positively with SSA (exception: very organic-rich soils) (Sokołowska, 2011). Greater SSA and sorption capacities decrease the substrate availability and thereby diffusive fluxes of solutes in soils.

Iron and aluminum oxides, hydroxides and oxyhydroxides (Fe/Al-O) (Kome et al., 2019) often form and predominate under acidic conditions and in strongly weathered soils, where soil weathering and base cation leaching has decreased the base saturation and soil pH (He et al., 2019; He et al., 2004). The influence of Fe/Al-O on diffusive fluxes is strongly related to the pH of the given soil and driven by their large SSA. **Fe/Al-O**, such as hematite, goethite, ferrihydrite, and boehmite (***Table 5***), form at later stages of weathering and have a particularly large specific surface area and therefore a very high sorption strength for organic matter and nutrients (Barrón & Torrent, 2013). Low pH levels increase the release of free Fe and Al ions promoting the precipitation of substances such as phosphate as Fe-phosphates (Bolan et al., 2005). Due to the remarkable sorption strength of Fe/Al-O and base cation leaching, base cations (K^+, Ca^{2+}, $Mg^{2+,}$ and Na^+) are replaced with acidic ions such as Al^{3+}, $Fe^{2+,}$ and H^+ (Ng et al., 2022). Therefore, in acidic soils with pH below 4.5, Al minerals dominate, thus increasing concentrations of mobile Al^{3+}. Further decreases in soil pH (around 3-4) causes Fe to dominate. Consequently, in forest soils with high cation exchange capacity, soil organic matter content, and clay minerals, the acid buffering capacity is also greater (Gruba & Mulder, 2015; Jiang et al., 2018; Tinker & Nye, 2000). Warm temperatures and heavy precipitation accelerate soil acidification through the leaching of base cations and

their exchange with protons and acidic cations. In this case, diffusion of nutrients is much lower with increasing buffering capacity and higher Fe/Al-O contents, because of strong electrostatic interactions with solutes and therefore due to decreased solute concentration (Hartemink, 2016).

Table 5. **Selected Fe/Al oxides, hydroxides and oxyhydroxides and their properties. CEC…cation exchange capacity (meq (100 g)$^{-1}$), SSA…specific surface area (m^2 g^{-1}). n.a. …not applicable**

Name	**Formula**	**CEC** (pH 7)	**SSA** (N_2, H_2O)	**AEC**	**Reference**
Imogolite	$Al_2SiO_3(OH)_4$	20-30	1540	n.a	(Kumari & Mohan, 2021)
Allophane	$Al_2O_3 \cdot (SiO_2)_{1.3\text{-}2} \cdot (2.5\text{-}3)H_2O$	30-135	100-2200	n.a	(Kumari & Mohan, 2021)
Hematite	α-Fe_2O_3	4-100	10-66	n.a	(Borggaard, 1983)
Maghemite	γ-Fe_2O_3	n.a	8-32	n.a	(Borggaard, 1983)
Goethite	α-FeO(OH)	4-100	13-94	5	(Borggaard, 1983)
Lepidokrokite	γ-FeO(OH)	n.a	30-221	5	(Borggaard, 1983)
Corundum	γ-Al_2O_3	n.a	140	n.a	(Amrute et al., 2019)
Boehmite	γ-$AlO(OH)_3$	n.a	89-366	n.a	(Amrute et al., 2019)

3.1.4 Sorption - Soil pH

Soil pH, i.e. the negative logarithm of the hydrogen ion concentration regulates nutrient availability through direct and indirect effects and due to rapid or rather long-term effects. Soil solution pH directly affects sorption via effects on the sign and magnitude of charge of the sorptive (solute) and of the sorbent (soil matrix constituents). When solution pH increases, hydroxyl and carboxyl groups of Fe/Al-O and SOM deprotonate, which increases the negative charge density promoting cation adsorption. Solutes may also underly

acid dissociation or hydrolysis reactions, causing strong pH-dependent sorption changes, e.g. for strong and weak acids such as phosphates ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) and organic acids, or zwitterionic compounds such as amino acids and peptides, and strong and weak bases such as ammonia/ammonium. Rothstein (2010) highlighted that adsorption to soil solids at soil pH is stronger for positively charged amino acids (Arg -arginine, Lys - lysine, His - histidine), whereas negatively charged amino acids (Glu – glutamate, Asp - aspartic acid) have the lowest adsorption potential. Diffusion of specific amino acids (acidic, polar, hydrophobic, basic ones) are particularly affected by soil pH as shown by microdialysis studies (***Table 7***). Therefore, diffusive fluxes measured in an acidic tussock tundra by Homyak et al. (2021) revealed that positively charged amino acids covered 68% of the total of 17 amino acids analyzed.

Indirectly soil pH also exerts multiple strong effects on soil nutrient availability, through its impact on soil weathering, CEC, base saturation, microbial activity and plant root development, and nutrient speciation. The ideal pH range of soils is considered to be between 6 and 7, representing the optimal pH for organismal activity and for the balanced availability of macro- and micronutrients (Eash et al., 2015). Biota also affect soil pH in their vicinity, e.g. in the plant rhizosphere. As an example, Comerford (2005) reported an increase in pH in the rhizosphere when nitrate was assimilated by plants. Plants consume H^+ or excrete OH^- for each nitrate that is taken up. The opposite happens during plant ammonium utilization. Rattan and Deb (1981) described the negative influence of high, neutral to alkaline, soil pH or $CaCO_3$ amendment in terms of zinc (Zn) and iron (Fe) transport via diffusion. At high soil pH organisms might also suffer from trace element limitations and phosphorus (P) deficiencies through P immobilization by precipitation as Ca-phosphates. Low soil pH, on the other hand, indicates a deficiency of base cations that plants require to thrive, such as Ca, Mg, and K, and the presence of increased concentrations of acidic elements such as Al, Mn, and Fe, which can become toxic at high levels (at pH <5.5 high concentrations of Al in soil). Finally, at extremely acidic soil pH values, many soil processes are slowed down, through the inhibition of microbial activities, of soil organic matter breakdown, nitrification, and nitrogen fixation.

3.1.5 Ion-exchange processes

Ion exchange processes are the second most important chemical reaction controlling nutrient availability in soils, because ions that are bound to soil particle surfaces become

available for plants and microorganisms via exchange mechanisms with other ions, released by the organisms themselves. Exchangeable cations and anions are balancing the negative and positive charges, respectively, associated with clay minerals, Al/Fe oxyhydroxides and soil organic matter by electrostatic attraction. Both cations and anions form ion pairs with weak bonds, resulting in the rapid replacement of one ion with another. The sorption strength of an ion to its exchange site is related to charge density and molecular size, with small, highly charged ions being more strongly bound than large, weakly charged ions. Thus, for cations, Al^{3+} has the highest ion-exchange strength and among anions PO_4^{3-} (Meetei et al., 2020). These affinity sequences are termed Hofmeister or lyotropic series and are for cations $Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+ > Li^+$. In this series, Al^{3+} has the largest valence and the smallest hydrated ion radius and is therefore bound the strongest. For trace and heavy metal cations the binding strength decreases from Pb > Cr^{3+} > Hg > As > Zn = Ni > Cd > Cu > Ag > Co (MINTEQ model description). However, for clay minerals such as illites or montmorillonite the series differs from the classical lyotropic series, with $K^+ > Ca^{2+} > Mg^{2+} > Na^+$ (Foscolos, 1968). For anions this series is $PO_4^{3-} > CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^- > OH^-$ (Kang et al., 2020).

Ion exchange processes are influenced by soil physicochemical parameters. Cation exchange capacity increases with an increase of organic matter content and clay content, and with clay mineral type – three-layer type (2:1) having greater CEC, and with an increase in soil pH. High cation- and anion-exchange capacities increase the buffering capacities of soils, but negatively affect solute diffusion fluxes, more strongly those of small ions and those with a high charge density.

Many of the nutrients that plants and soil microbes adsorb are positively charged ions, making the soil CEC a strong driver of nutrient availability (Havlin, 2013). Cation exchange capacity (CEC) describes the ability of negatively charged soil components (clays, SOM) to attract, retain, and exchange cation elements. Both clay, and soil organic matter, strongly influence the cation exchange capacity of soils by increasing CEC. A high CEC in turn decreases the movement and uptake of nutrients in soils because more nutrients are attached to the soil mineral surfaces rather than being freely available in the soil solution, where soil organisms and plants can access them directly. In addition to clay and humus content, soil pH also plays an important role in changing the cation exchange capacity of soils (Eash et al., 2015). CEC is proportional to soil pH, with increasing soil pH increasing soil CEC. Base saturation expresses the percentage of base cations relative to cation exchange capacity. Similar to CEC, base saturation is proportional to soil pH (Havlin, 2013)

and positively affects the diffusion rates of base cations. Base saturation is considered to be an important estimate of soil fertility (Johnston & Karamanos, 2005).

There has been a bigger focus on studying soil CEC over anion exchange capacity (AEC), mainly because soil components are predominantly negatively charged (Nunes & Mulvaney, 2021; Pansu & Gautheyrou, 2006). Anion exchange capacity (AEC) describes the density of positively charged soil components, mainly deriving from protonated peptidic structures and rarely from variable charge clays. Some nutrients come in the form of anions such as sulfate, phosphate, chloride, and nitrate. These nutrients tend to be leached from soil to groundwater as they are not attracted to clay minerals (Eash et al., 2015), and since the AEC in soils is usually low, representing only 10% of that of CEC. The anion exchange capacity is negatively correlated with soil pH, i.e. at pH <6, soils dominated by kaolinite clay (1:1 type clay minerals) have higher anion exchange capacity than montmorillonite- or illite-dominated soils (2:1 clay minerals). The pH effect is also caused by greater protonation of SOM-related amino groups at lower soil pH, increasing a soils' AEC. Moreover, Fe/Al-Oxides become positively charged at low soil pH, expressing increasing AEC. The increase in the concentrations of Fe/Al-oxides results in adsorption/precipitation of PO_4^{3-} (Bolan et al., 2005).

3.2 Controls of concentration gradients: source – sink relations (SSR)

Concentration gradients are found in the vicinity of roots, fertilizer granules, microbes and at the topsoil (Staunton, 2008). Concentration gradients of nutrients (or any kind of solute) have multiple causes, many of them operating in parallel and simultaneously. These are shortly listed in ***Table 6*** classified as source and sink processes, and processes cancelling the concentration gradients.

Table 6. **Source and sink processes governing the establishment, or eradication, of concentration gradients, which drive diffusive fluxes in soils.**

Component	**Processes**	**Drivers**
SOURCE		
- Fertilizer	Fertilizer amendment	Agricultural activity
- Desorption	Desorption	Counterion secretion (H^+, OH^-, bicarbonate, carboxylates), buffer capacity
- Dissolution	Dissolution	Inorganic chemical processes (weathering), organic acids/siderophores
- Decomposition	SOM and litter recycling	Microbial activity, extracellular enzymes, intracellular catabolism, buffer capacity
- Biomass turnover	Death of microbes/roots/soil animals	Microbial/plant activity, senescence, grazing, release of organic metabolites
SINK		
- Sorption	Sorption	Mineral and organic phase properties, pH
- Precipitation	Precipitation	pH, counterions

- Uptake	Microbial and plant uptake	Biological demand and growth
- Leaching	Percolation	Rainfall, seepage
MASS FLOW	Pressure-driven water flow mixing soil water and cancelling depletion shells	Rainfall, plant transpiration

SSR cause increased concentrations of solutes originating from a source distant from a sink, while sinks cause the depletion of nutrients in their vicinity. Both sources, and sinks can be biotic and/or abiotic soil system components (***Table 6***). Sources-sinks relations must be in balance so that the input of nutrients does not exceed the output and vice versa.

In terms of diffusion theory, sources or sinks are abbreviated and defined with the term *R*, the sign indicating the source (+R) or sink (-R) nature of R. Sink activity causes the development of depletion shells (zones) in close vicinity of the sink, when the nutrient delivery via mass flow does not fully meet the nutrient/solute demand of the absorbing cells/tissues/organisms (microbe, root); in this case nutrient uptake by the organism causes a drop in nutrient concentration around the absorbing surface. The buffer power of a soil here refers to the capacity of a soil to replenish nutrients into the soil solution (Van Rees et al., 1990). Interestingly the buffer behavior of a soil can differ during adsorption and desorption phases, termed hysteresis, e.g. for phosphorus.

3.2.1 Source strength of desorption and dissolution

Dissolution is a physiochemical process resulting in a solution by dissolving the solute in a solvent. Furthermore, mineralization and immobilization are important biochemical processes that transform nutrients into available forms for plant uptake. These processes influence the population and activity of biotic factors.

The bioavailability of nutrients is controlled by exudation of organic acids and siderophores by microbes and plants (low molecular weight acids). Organic acid exudation performed by plant roots depend on the bioavailability of P, Mn, and Fe as well as the tolerance to Al toxicity (Comerford, 2005).

The phenomenon called *hysteresis* happens when sorption and desorption concentrations are not in equilibrium regardless of simultaneous measurements or temperature conditions. Sorption and desorption are similar but not identical, the desorption

process is irreversible. This phenomenon is happening due to differences in time and energy between sorption and desorption processes (Fredriksson & Thybring, 2018). (Chorover & Brusseau, 2008) found that sorption hysteresis is proportional to contact time.

Desorption reaction is driven by abiotic (H^+ or OH^- etc.) and biotic (root exudates enhance desorption of contaminants/nutrients) means (Comerford, 2005; LeFevre et al., 2013).

3.2.2 Source strength of mineralization and microbial/root turnover

Soil organic matter (SOM): is made up of any plant and animal litter at different stages of decomposition that can be produced by microbes. SOM constitutes a large reservoir of plant essential nutrients (e.g. N, P, S, K, Ca, Mg) and of trace elements. Chemically, SOM is on average composed of 50% carbon (C), 39% oxygen (O), 5% nitrogen (N), 5% hydrogen (H), 0.5% phosphorus (P) and 0.5% sulfur (S) (Eash et al., 2015). This also produces a relatively constrained stoichiometry of C:N:P and S in global soils, of 287:17:1 for soil elements and 42:6:1 for soil microbial biomass (Xu et al., 2015; Xu et al., 2013). The nutrient elements N, P and S are covalently bound as organic nutrients (elements) in the SOM matrix, while others such as the cationic alkali and Earth alkali elements are bound via ion-exchange to SOM. However, each soil is different and therefore its elemental OM composition may vary across soils.

The SOM quantity greatly differs between soil types and sites. Clayey soils commonly are higher in SOM, because of their higher SSA, allowing greater sorption and stabilization of SOM and the elements making up SOM, and also retain more nutrients via sorptive processes, due to their higher ion-exchange capacity than sandy soils (Eash et al., 2015). The quantity and composition of soil organic matter are influenced by plant cover, soil management, as well as by the composition and activities of soil microbial communities, but also by a variety of other chemical and physical soil properties, such as cation exchange capacity and pH (Picariello et al., 2021). In relation to land use, maize and wheat yields are boosted with higher soil organic carbon levels (at ~ 2% SOC) (Oldfield et al., 2019).

High amounts of SOM are found in forested areas where the surface of the soil contains more leaf and twig litter due to less soil disturbance i.e. through the lack of tillage activities as performed in many croplands (Bot et al., 2005). Temperature and moisture are additional parameters that are considered to affect SOM content. High temperatures promote plant growth while also organic matter decomposition, therefore, for instance, there is little

organic matter found in tropical rainforests due to low organic matter accumulation as microbial activity is increased. Moreover, moisture is positively correlated with soil organic matter content, thus wetter environments display more organic matter (McKenzie et al., 2004; Osman, 2013).

Soil organic matter forms a continuum of organic matter species with different turnover times. This is due to differences in organic source materials, climate, geology, and land use, a result of the continuous biological breakdown of OM at various stages of SOM development and their differential stabilization. SOM is composed of the following "coarse" fractions and all kinds of intermediates:

1. The living part that constitutes the soil microbial biomass and comprises 1-5% of total SOM. Living organisms comprise plant roots, fungi, algae, and other micro-and macroorganisms. It is one of the most important fractions because it is a continuous source of plant nutrients, and serves other important functions (Reddy, 2016).
2. Fresh residues which are derived from plants, soil microbes and fauna, comprising ~10% of total SOM. The fresh residue consists of freshly decayed organic matter that begins to decompose immediately because it is not yet occluded in the soil (Osman, 2013).
3. The active fraction that is soil organic matter at an early decomposing stage which makes up 33-50% of total SOM. The active fraction includes the organic matter that is currently decomposing and that is used and transformed by microorganisms.
4. The stabilized fraction that is humus and consists of 33-50% of total SOM (Reddy, 2016). The stable fraction of organic matter results from the continuous breakdown of detritus that forms a more complex OM called humus. Humus is composed of humic substances i.e. fulvic acids, humic acids, and humin. Since humus is a chemically complex fraction of organic matter, it cannot be directly used as an energy source for microorganisms therefore it remains in the soil for a long time.

Soil microbial biomass (SMB) comprises the living constituent of the SOM where microbial processes take place and plant available nutrients are stored (Horwath & Paul, 1994). Microbial biomass is strongly positively linked to SOM content and constitutes a continuous supply of labile nutrients to plants through microbial turnover (Yao et al., 2000). More than half of total microbial biomass is located in the top 25 cm of the soil profile (Frey, 2007). It mostly includes soil bacteria and fungi, which secrete most C-related enzymes and turn organic residues into carbon dioxide and plant available nutrients, they are using for their own growth (Luan et al., 2021; Wardle et al., 1999). Consequently, soil microorganisms

are indicators of soil fertility, plant development, and carbon cycling (Jiang et al., 2013; Yan et al., 2021). Physical properties are affecting microbial biomass as the amount and diversity are positively correlated with soil pH and the clay content of a soil (Dalal, 1998; Malik et al., 2018; Xiao et al., 2021). In clayey soils, high amounts of microbial biomass are found, because clay-textured soils retain more water and contain more organic matter which is an essential energy source for microbial decomposition.

Microbial biomass is both a sink as well as a source of labile C, N, P, and S in soils (Dalal, 1998). In soil science, the term labile depicts a substance or a form of an element that is easily decomposed by microorganisms or is plant available (Foth, 1978). Although microbial biomass accounts for only a small fraction (less than 5 %) of the total soil organic matter, the turnover rate of microbial nutrients are at least an order of magnitude faster compared to the remaining fractions of SOM (Dalal, 1998). The reason for such rapid turnover rates are owing to their simple structure and high quality of carbon and nutrients (Wang & D'Odorico, 2013), as well as viral lysis and grazing by soil fauna. The labile pool of a nutrient is adsorbed on the solid phase of soil serving as a directly available pool of nutrients to plants (Chesworth, 2008). However, labile C, N, and P are also highly important compounds in soils to sustain the soil microbiota (J. Chen et al., 2021). Labile carbon is a direct source of energy for microbial biomass and an essential compound due to its role of regulating soil respiration and microbial heterotrophic energy conservation (Fu et al., 2020; Glanville et al., 2016). Further, low molecular weight (LMW) carbon compounds are significant because of their rapid flow through soil solution and are considered to control soil CO_2 efflux (Glanville et al., 2016; Hees et al., 2005).

Microbial activity describes the microbiological processes taking place in soil systems. These processes are performed by microorganisms that turn organic compounds into inorganic, readily available nutrients for plant uptake (Chen et al., 2003; Roy et al., 2006). Microbial activity is most concentrated where labile organic matter is highly abundant such as in the rhizosphere due to an abundant energy and mineral supply (Adhya et al., 2018; Gliński & Lipiec, 2018) that helps microorganisms in respiration and subsequently growth. There are numerous factors controlling microbial activity, such as soil moisture, temperature, soil aeration, organic carbon – as a food source, and pH. Taking into consideration that temperature positively correlates with microbial activity, a direct effect of temperature on soil moisture and microbial activity shows that elevated temperatures coupled with a dry soil do not lead to high microbiological processes (Wang & D'Odorico,

2013). Optimal moisture contents (i.e. 60% water-filled pore space) promote transport and supply of substrate to soil microorganisms through diffusive fluxes (Hakeem et al., 2016; Wang & D'Odorico, 2013). In addition to soil moisture, soil aeration plays a significant role in microbial activity (Bot et al., 2005) i.e. wet soils display low aeration values thus less oxygen remains for respiration that in turn results in low microbial decomposition processes (Wang & D'Odorico, 2013). Physical soil properties like texture, bulk density and pore size distribution also influence microbial activity. High microbial activity is present in small pore sizes ranging from 0.2 to 15 μm in diameter (Frey, 2007), hence fine textured clayey soils serve as a great nutrient supply as well as living habitat for microorganisms (Li et al., 2019).

Microbial SOM decomposition: Microorganisms decompose OM through mineralization and thereby release essential plant nutrients and trace elements (Bot et al., 2005; Eash et al., 2015). The rates of organic matter decomposition influence the nutrient supply, which in turn are accelerated by high temperatures, water availability, and organic substrate (Henderson, 1995). For plants to be able to take up nutrients, the breakdown of organic matter is needed. For fast decomposition, microorganisms require optimum moisture levels, temperature, and a pH range between 6.5 - 8.5. For instance, lower soil moisture content results in lower diffusion rates for the decomposition of compounds. Microbial biomass decreases towards low pH soils (pH less than 6.2), due to increased investment of energy to cope with soil acidity, while plant and soil organic matter content increases due to slower mineralization rates in acidic soils (Bian et al., 2022; Malik et al., 2018; Xiao et al., 2021). However, fungi can still decompose complex organic compounds at pH < 5, where bacterial activity diminishes and only acidotolerant or acidophilic microorganisms can thrive. The rate of SOM decomposition may be altered because changes in nutrient availability alter soil microbial community composition and activity (Schmidt et al., 2011). Fine-textured soils are commonly associated with high organic matter content and lower mineralization rates (Prescott, 2005). The reason for this is the physical protection of organic matter from decomposer organisms (Bachmann et al., 2008), through physical sorption of organic matter on clay minerals or its entrapment in pores or in aggregates that make organic matter inaccessible to microbes. Clay minerals physically and chemically protect SOM via sorption that stabilizes SOM against microbial activity. Physical protection occurs due to inaccessibility of microbes to reach SOM as clay particles form small pores. Depending on soil texture and pore size distribution, resource access and use by the microbial community is restricted in pores smaller than 0.8 μm (Frey, 2007). Chemical protection occurs due to

their high charge and specific surface area (SSA) resulting in less efficient microbial enzyme decomposition of OM when SOM is sorbed to clay minerals (Wei et al., 2014). Iron oxides are similarly linked with SOM stabilization through adsorption mechanisms and promote OM stabilization and thereby reduce biological degradation (Eusterhues et al., 2014). This derives from the fact that Fe oxides have high sorption capacities due to their large surface area and this might also inhibit SOM decomposition at acidic pH levels (Hu et al., 2020). Decomposition is further affected by the amounts of N and P present for microbial processes (Hartman & Richardson, 2013). C, N, P and S influence the cycling of each other due to their linkage in SOM. Several authors e.g. Manzoni et al. (2010); Reddy (2016) showed that a low substrate C:N ratio (below 24:1) results in a high flux of N that microorganisms mineralize into inorganic N for plant uptake.

Soil microbial community composition refers to the features of a community of microorganisms, their diversity of species, and/or abundance of its members in a given soil (Azarbad et al., 2014; Bier et al., 2015). Not only the microbial biomass is concentrated in the top 10-25 cm of soil but so are microbial diversity and community composition (Frey, 2015). Soil microbial community composition is strongly influenced by soil chemical and physical properties and by plant species composition (Bettermann et al., 2021). Microbial activity also depends on the composition of microbial communities (Morris & Blackwood, 2015) because it shapes the functions it will carry out, meaning that highly diverse and abundant communities are highly functionally redundant and will likely be more active. It is to be highlighted that the soil N cycle is closely related to the characteristics of microbial communities (Z. Chen et al., 2021; Deng et al., 2016). The reason for this is that the mineralization and further transformations of inorganic N involves the work of specialist groups (ammonium and nitrite oxidizers) (Merrington et al., 2006). Microbial diversity shifts to higher fungal abundances at low and at high moisture conditions as opposed to bacteria and this results in more organic matter decomposition by fungi under such conditions. Fungi have also been reported to be more tolerant to withstanding extreme conditions Wang and D'Odorico (2013). Furthermore, Crowther et al. (2019) highlighted that fungi are slower at decomposition, but in comparison to bacteria they are able to decompose chemically complex organic matter. It is interesting to point out that trees are growing better in fungi rich soils and grassland is associated with bacterial presence and faster nutrient cycling. The results from the synthesis of more than 45 articles from

Table 7 showed a larger increase in diffusive fluxes in croplands than in grasslands and forests. For instance, in the study from Inselsbacher et al. (2011) flux rates measured in agricultural soils were 96 nmol N cm^{-2} h^{-1} for NO_3^- whereas in forest soils flux rates were similar with amino acids and ranged between 27.1-40.3 nmol N cm^{-2} h^{-1}.

Soil enzymes: SOM decomposition, particularly the initial steps targeting high-molecular weight SOM compounds, is largely mediated by soil enzymes, enzymes secreted into the soils or being cell-wall bound by microbes and plant roots. These extracellular enzymes play a key role in the regulation of the biogeochemical cycles of C, N, P and S. Microbes secrete extracellular enzymes when nutrients and energy are not enough for plant growth (Luo et al., 2017). Fresh plant litter has been shown to stimulate microbial exoenzyme activity, serving as one of the main decomposition agents as well as a crucial regulator of nutrient bioavailability in soil systems (Buckley et al., 2019). Extracellular enzymes are secreted by decomposers to the outside environment and turn complex organic matter into inorganic compounds such as sugars, amino acids, ammonium, phosphate etc. The role of extracellular enzymes is to recycle nutrients from litter and accumulated SOM (Caldwell, 2005). Hydrolytic enzymes use water to breakdown larger molecules such as carbohydrate and protein whereas oxidative enzymes rely on oxygen (oxidase) or hydrogen peroxide (peroxidase) to degrade lignin and humics to gain C, N, and P (Burns et al., 2013; German et al., 2011).

3.2.3 Source strength of fertilization

Fertilizers are an important source to sustain soil fertility and nutrient balance in soils. They consists of any substance containing major plant elements that improve plant growth and/or boost productivity by supplying more vital compounds for usage by plants (Jones Jr, 2012). Many types of fertilizers exist but the main macronutrients present in common fertilizers are Nitrogen, Phosphorus, Potassium, together termed as NPK fertilizer. There are also secondary macronutrients present as Calcium, Magnesium, Sulfur that are also important. Lastly, micronutrients are also present as Iron, Copper, Zinc…

Some fertilizers are derived from inorganic (synthetic) or organic (natural) materials, and depending on the amount needed, fertilizers can get released in the soil/plant system as single or multiple elements (i.e. NPK are a three-component fertilizer). Urea as a source of nitrogen and KCl are among the most used solid mineral fertilizers. Plant and animal residues of agricultural or forestry origin such as manure, compost or biochar constitute one of the

few fertilizers based on materials of organic origin. Increased environmental pollution due to inadequate fertilizer use causes N and P accumulation in soils, runoff into surface water and leaching into groundwaters leading to eutrophication. High accumulation of N in soils results in soil acidification. In order to buffer the pH of acid soils, liming is required to set the pH levels back to desired levels (Wikipedia contributors, 2023).
Slow and controlled release fertilizer are a type of fertilizer and are proven to be efficient against overfertilization. But, combining micro- and macronutrients fertilizers by coating in various nano- and micro- materials help in releasing the desired compounds efficiently in soil systems (Umar et al., 2022).

3.2.4 Sink strength of sorption/precipitation

The most important sinks from abiotic factors are sorption, precipitation, leaching, and mass flow. The sinks of biotic factors include microbial and root uptake. Sorption is mentioned and described in detail in chapter 3. Drivers and controls of diffusion of solutes in soil. It is described as the binding of charged species from soil solution to a solid surface. Sorption occurs through adsorption and precipitation. Sorption processes are influenced by physical, chemical as well as biological controls. CEC and AEC play a significant role in controlling sorption processes due to positive and negatively charged amino acids being strongly sorbed than neutral amino acids. The positive and negative charges of amino acids are related to soil pH therefore influencing sorption (Rothstein, 2010). Thus, as stated earlier in the text charge density, molecular size are related to sorption strength which is inversely proportional to mobility of the solutes. A difference between sorptive strengths are NO_3^- which has a high mobility compared to PO_4^- which is less mobile.

3.2.5 Sink strength of microbial/root uptake

Competition for nutrients are common between microbes and plants because of (1) The limiting nutrients (mainly N and P); (2) Formation of diffusion shells around roots because of the nutrients taken up by plants; (3) The large deposit of easily available carbon favors high microbial activity and growth in the rhizosphere thus leading to higher microbial uptake and immobilization.

Microbe-plant associations are not only competitive but symbiotic as well. The mutualistic relationships are based on fungal (mycorrhizae), or bacterial interactions

(diazotrophs and associated microbiota - plant growth promoting rhizobacteria PGPR) with plant roots (Kuzyakov & Xu, 2013). Mycorrhizae constitute a plant-fungal hyphae symbiotic relationship with the main purpose of exchange of mineral nutrients that are beneficial for plants with lipids and sugars that are beneficial for fungi. Benefits of mycorrhiza include (1) a better nutrient transport through hyphae compared to diffusion, (2) more space for soil exploration due to small hyphae (<0.01 mm) compared to plant root (0.1 – 1 mm), (3) reduced organic matter costs, plants invest 4-20% of gross primary production to support mycorrhizal hyphae (Chapin et al., 2011). Mycorrhizal roots extend and manage to assimilate higher fluxes of nutrients over longer periods of time long after diffusion shells develop around the roots which are due to rapid non-mycorrhizal plant consumption of mineral compounds (Smith et al., 2001). As a result of C supplied by plant roots, diazotrophs are responsible for assimilating atmospheric nitrogen (N_2) (e.g. rhizobia and Frankia) and turning into ammonia (NH_3) (Kuzyakov & Xu, 2013).

3.2.6 Mass flow cancels source sink effects periodically

Mass flow supplies easily available and abundant nutrients to plant roots but the nutrients that are limiting are transported through diffusion, e.g. N, P, K. The mechanism of mass flow as transport of nutrients is based on water movement induced by plant transpiration and soil solution concentration (Oliveira et al., 2010; Oyewole et al., 2014).

Rainfall redistributes nutrients and fills up diffusion depletion zones that surround roots. Because water is transported vertically to lower depths, this water movement causes diffusion depletion zones to be rapidly eliminated (Chapin et al., 2011).

3.3 Controls of diffusive path length

The effective diffusion coefficient (D_e) describes diffusion through the pore space of porous media such as soils. The D_e coefficient for transport through the pore space is estimated as follows:

Equation 6. The effective diffusion coefficient (1)

$D_e = \frac{D\,\varepsilon_t\,\delta}{\tau}$, where

- D is the diffusion coefficient of the solute in free soil solution, the liquid filling the pores,
- ε_t is the porosity available for transport (dimensionless),

- δ is the constrictivity (dimensionless),
- τ is the tortuosity (dimensionless).

The fraction of porosity available for transport equals total porosity minus the pores which are not accessible to the diffusing solute (size restrictions) minus dead-end pores (i.e., pores without connection to the rest of the pore system). Constrictivity describes the deceleration of diffusion by increasing viscosity in narrow pores, due to greater proximity to the pore wall (a function of pore diameter and the size of the diffusing solute). Tortuosity refers to the ratio of the diffusivity in free space (solution) to the diffusivity in a porous medium, the latter being governed by geometry. In its simplest form tortuosity represents the ratio of the length of a curve (C) to the distance between its ends (L): $\tau = C/L$. Alternatively the effective coefficient has been expressed as

Equation 7. The effective diffusion coefficient (2)

$$D_e = D_L \, \theta_L \, f_L \, \frac{dC_L}{dC}$$, where

- D_L is the diffusion coefficient in liquid (see above, D),
- θ_L is the fraction of soil volume occupied by soil water, equivalent to volumetric water content (VWC), representing the cross-sectional area for diffusion,
- f_L is an impedance factor, related to the geometry and tortuosity of the soil pore network,
- C_L is the concentration in soil solution, and
- $\frac{dC_L}{dC}$ is the solute sorption on the soil solid matrix.

In this equation the impedance factor becomes important, which is linearly related to bulk density.

3.3.1 Soil density, porosity, and pore size distribution

Porosity is the fraction of the total soil volume that is comprised by the pore space and typically ranges between 0.3 to 0.35 in mineral soils and 0.7-0.9 in organic soils (Nimmo, 2004). Soil **bulk density**, which reflects the degree of compaction of a soil, is negatively correlated with soil porosity. The bulk density of a soil, i.e. the dry weight of soil divided by its volume, comprises both, solid particles and pores, and ranges between 0.6 to 1.6 g cm^{-3}, depending on soil texture, compaction, and organic matter content. In contrast, the **particle density** only represents the solid volume, with typical particle densities in soils ranging from 2.60 to 2.75 g cm^{-3} for mineral particles. The pore system acts as a conduit for water to enter and exit the soils, by retaining or draining the water based on the size of the pores, enabling diffusive fluxes and mass flow of solutes in soils (Eash et al., 2015). Some

physical soil properties such as soil structure, hydraulic conductivity, porosity, macroporosity, as well as diffusion of solutes are strongly linked to soil bulk density (Fujikawa & Miyazaki, 2005). The parameters that most importantly drive bulk density and porosity in the first few meters of the topsoil are clay content and soil organic matter content (Chen et al., 1998). Helliwell et al. (2017) showed that proliferation of the plant root system influences soil porosity, particularly by promoting preferential flow through previous root channels. Bulk density is negatively correlated with aggregate stability and size (Amézketa, 1999). Moreover, soil organic matter (SOM) promotes biological activity and soil structure and increases soil porosity and the proportion of air-filled pore space, but decreases bulk density (Sparling et al., 2000).

Pore size distribution is also a major determinant of potential solute fluxes, with larger pores promoting diffusive fluxes and mass flow of solutes compared to smaller pores, which hold water and solutes more tightly (Nimmo, 2004). **Pore sizes** are specified by their effective radius *r* of the pore body or the pore neck, and by capillarity this relates to the matric pressures at which breakages of the water films occur. The pore-size distribution then represents the relative abundance of each pore size in a representative volume of soil. According to (Cameron & Buchan, 2006), macropores are greater than 75 μm in diameter and are most commonly found between aggregates. They are too large to exert any significant capillary force on water films, are generally air-filled at field capacity as they drain freely by gravity, and allow rapid movement of water, solutes, and air. Mesopores have diameters of 30-75 μm and are usually found within structural aggregates. They are the largest pore size class filled with water at field capacity, where suction is required to remove water from them. This also leads to slower diffusive and mass fluxes of solutes retained in mesopores. Micropores (5-30 μm) hold water by strong capillary forces, and while the water is still plant-available, solute movement is slower and happens only by diffusion. Cryptopores (0.007-0.1 μm) and ultramicropores (0.1-5 μm) are too small to play a significant role for soil nutrient diffusive fluxes.

3.3.2 Soil structure and aggregation

Soil structure refers to the spatial arrangement of the solid soil particles and of the interspersed pore spaces (Marshall et al., 1980). **Aggregates** form when soil particles interact with each other by rearrangement, flocculation, and cementation. Aggregation is promoted by precipitation of minerals (e.g., oxyhydroxides and carbonates), by biological activity

gluing particles together (with extracellular polymeric substances, fungal hyphae, and glycoprotein), and by attraction or repulsion processes by multivalent cationic bridging between clay minerals and organic compounds (Bronick & Lal, 2005). This soil structure is highly dynamic and responsive to biological, chemical, and physical controls, leading to structural rearrangements of soil particles, soil organic matter, and the pore space. An ideal soil structure is associated with a great volume of pores in such sizes that enables water to be stored in the soil, but at the same time allows for good drainage, facilitating air- and waterflow, improving soil porosity, decreasing erodibility, and promoting root growth and development (Eash et al., 2015). The presence of stable macro-and micro-aggregates indicates a good soil structure (Amézketa, 1999), aggregation through interaggregate spacing increasing porosity to 0.5 and greater (Nimmo, 2004). Bronick and Lal (2005) showed that the soil flora and fauna promote the formation of these aggregates and of organo-mineral complexes. Microbial activity may regulate soil organic carbon (SOC) storage by forming microaggregates, protecting soil organic matter from decomposition (Gougoulias et al., 2014). High levels of SOC and humus improve soil aggregation and aggregate stability, as well as increase porosity (Bot et al., 2005). Microbial communities and their metabolic activities promote C storage in macro-aggregates (> 0.25 mm) (Lu et al., 2021). Clay mineralogy also affects aggregate stability, due to clay minerals having either large (smectitic clays) or small specific surface area (SSA), variable cation exchange capacity (CEC), and thereby different physicochemical binding capacities (Amézketa, 1999). (Hartmann et al., 1998) showed that there is a link between soil structure, hydraulic conductivity, and cation exchange capacity, as well as cation transport processes. The slower the water moves through the soil pore space the more chemical/exchange reactions can take place in the soil pore space, increasing the ion storage capacity, but slowing down diffusive processes.

3.3.3 Soil moisture, water-filled pore space and viscosity

Soil water content, especially in terms of the **water-filled pore space** (WFPS) of soils, is considered one of the most important factors controlling diffusive fluxes in soils (Jämtgård et al., 2018). Indeed, Manzoni et al. (2016) confirmed that the number of water-filled pores limits diffusion. The aqueous phase in the form of water films inside the soil pore space becomes discontinuous in dry soils. Because of this, diffusion of solutes becomes limited, the cross-sectional area that is available for diffusion is reduced, but concurrently

the effective path length increases (Müller et al., 2023). In other words, as soils dry it becomes increasingly difficult for solutes to reach the root surfaces, and **tortuosity** increases. Soil moisture content is not equally distributed in soils, and the water-film thicknesses can range in size and therefore can have a significant impact on solute and colloidal transport between the water menisci (Bachmann et al., 2008). This also causes the phenomenon that the impedance factor f_I decreases linearly with decreasing soil water content, expressing $f_I = \frac{De}{Dw\ x\ VWC}$. Effective diffusivity therefore relates to diffusivity in water times the volumetric soil water content (VWC), and this is proportional to texture and SSA (Moldrup et al., 2001). The effective diffusion constant of Zn, e.g., increased hyperbolic with VWC, with tortuosity being least at a bulk density of 1.3 g cm^{-3} (Warncke & Barber, 1972a, 1972b). Tortuosity increased towards lower and higher soil moisture contents, by deactivating and/or activating diffusive flow paths, respectively. Recent developments in terms of pore system characterization (microCT; micro-computed tomography) and soil physics modeling have greatly enhanced the capabilities to understand and model the internal structure and function of soils (Zachara et al., 2016). This has again lend support to better understand tortuosity as related to the complexity of pore geometry in porous media, showing differences and commonalities in the proxies and calculations of tortuosity (Zhang et al., 2021). Here tortuosity estimates increased from geometric ones through diffusive to fluid flow proxies, and generally decreased as porosity increased (Zhang et al., 2021). Tortuosity models are distinct and therefore cannot be used interchangeably (Ghanbarian et al., 2013; Zhang et al., 2021). Given the time-consuming and labor-intensive procedure to measure the effective diffusivity in soils and thereby characterize tortuosity, the search for simpler solute diffusion tortuosity models is still ongoing (Chou et al., 2012). Further, the **viscosity** of water close to clay mineral surfaces is higher than that of soil water in large pores, due to strong matric forces, which reduces solute diffusion in dry soils and in finer pores.

Table 7. **Overview on the application of microdialysis in soil systems sourced from (Buckley et al., 2020) and updated. *flow rate measured in µL min-1, fertilization yes/non.**

Author (Year)	Solutes	Biome	Management	Location	Flow rate*	Perfusate	Fertilization	Dry-rewet	Notes
Miró and Frenzel (2003)	Cl^-	Temperate	Forest	-	200	Milli Q water KNO_3	N	dry	First utilization of microdialysis to determine Chloride in soil samples.
Miró and Frenzel (2004)	Cl^-	Temperate	Agricultural	-	2	Water, KNO_3	N	moist	Addition of an electrolyte (0.25 mol L^{-1} KNO_3) as a perfusate enhanced the dialysis rate of chloride.
Miró et al. (2005)	Metal ions (Pb, Fe)	Temperate	Grassland	Austria	2	0.01 M $CaCl_2$	N	moist	First study of metal ions sampling using MD in interstitial/pore soil water.
Sulyok et al. (2005)	Oxalate, citrate	Temperate	Grassland	div. Austria	2	0.1 M $NaNO_3$	N	moist	Better recoveries (>83%) can be obtained by lowering the flow rate to ≤1.0 µl/min but leads to analytical disturbances. Metal contaminated soils; low microdialysate concentration due to adsorption/immobilisation of neutral organo-metallic complexes. Non-metal contaminated; highest microdialysate concentration.
Miró et al. (2010)	Metal ions (Cd, Pb, Cu, Ni)	Tem-perate	Grassland	Arnoldstein	2	0.01 M $CaCl_2$	N	moist	Microdialysis technique proved to be able to measure moisture levels as low as 50% (suction cups, 70%).
(Inselsbacher et al., 2011)	NH_4^+, NO_3^- and 12	Boreal	Forest Agricultural	Umeå, Sweden	5	Milli Q water	Y/N	moist	Plant available amino acids more prominent in microdialysis

	amino acids								results than lysimeter. High perfusate flow rate (10 µL min^{-1}) decrease relative recovery (10-20%)
(Inselsbacher & Näsholm, 2012b)	NH_4^+, NO_3^- and 12 amino acids	Boreal	Forest Agricultural	Umeå, Sweden	5	Milli Q water	Y/N	moist	Smaller compounds are more susceptible to increase in diffusive fluxes of N with increasing soil temperature. At lower temperatures, amino acids are available for plant uptake in the total N supply.
(Inselsbacher & Näsholm, 2012a)	NH_4^+, NO_3^- and 16 amino acids	Boreal	Forest	Åheden, Sweden	5	Milli Q water	N	moist	Organic N contributes 74-89% to total N flux in boreal forest soils, NH_4^+, and NO_3^- only 5-15%.
(Rosende et al., 2013)	Pb	Temperate	Agricultural	Mallorca, Spain	2	UBM fluid	N	dry	First application of automatic microdialysis sampling of Pb bioaccessibility using UBM fluid as a perfusate.
(Cocovi-Solberg et al., 2014)	Pb	Temperate	Forest	Austria	2	0,43 M AcOH	N	dry	Sampling of Pb using microdialysis as a front end to electrothermal atomic absorption spectrometry.
(Inselsbacher et al., 2014)	NH_4^+, NO_3^- and amino acids	Boreal	Forest	Rosinedal, Sweden	5	Milli Q water	Y/N	moist	In early spring more diffusive N fluxes available for growing roots due to frequent freeze/thaw and drying/rewetting cycles that affect N turnover.
(Oyewole et al., 2014)	NH_4^+, NO_3^- and amino acids	Boreal	Forest	Rosinedal, Sweden	1	Milli Q water Dextran	N	moist	Lower diffusion of N rates in soil than solution. Dextran used to induce mass flow by lowering the

									osmotic potential of perfusate.
(Shaw et al., 2014)	NH_4^+, NO_3^- and amino acids	Temperate	Grassland	United Kingdom	5	Milli Q water	Y/N	moist	Solute diffusion is decoupled from concentration since it is affected by various physical properties (moisture content, tortuosity factor, soil texture, etc.) that influence solute transport through soil.
(Brackin et al., 2015)	NH_4^+, NO_3^- and amino acids	Subtropical	Agricultural	Queenslan d, Australia	5	Milli Q water	Y	moist	The fluxes of inorganic N are much higher in fertilized soil and the plants cannot assimilate all the nutrients which result in N leaching due to inefficient fertilizer application.
(Oyewole et al., 2016)	NH_4^+, NO_3^- and amino acids	Boreal	Forest	Rosinedal , Sweden	5	Milli Q water	Y/N	moist	Regardless of season and fertilizer management, amino acids dominate the N pool in boreal forest soils.
(Brackin et al., 2016)	NH_4^+, NO_3^- and amino acids	Subtropical	Agricultural	Queenslan d, Australia	5	Milli Q water	Y	moist	Traditional soil extracts (using water and/or KCl) are less accurate in measuring N pools in soils (70% amino acids found in unfertilized soil using microdialysis and ~40 % amino acids by soil extracts).
(Brackin et al., 2017)	NH_4^+ and NO_3^-	Subtropical	Agricultural	Queenslan d, Australia	5	Milli Q water	Y	moist	MicroCT imaging combined with microdialysis showed accumulation (NO_3^-) and depletion (NH_4^+)

									of nutrients in the rhizosphere.
(Buckley et al., 2017)	NH_4^+, NO_3^- and amino acids	Boreal	Forest	Rosinedal, Sweden	5	Milli Q water	N	moist	Two microdialysis membrane configurations were compared, the longer membranes (increased surface area) resulted in greater overall N recovery
(Demand et al., 2017)	Phosphate	Temperate	Forest Agricultural Grassland	Germany	2	10 mM KNO_3	N	moist	First microdialysis analysis to mimic phosphate supply processes in soils.
(Leitner, Homyak, et al., 2017)	NH_4^+, NO_3^- and amino acids	Subtropical	Grassland	California, USA	5	Milli Q water	N	rewet	Emissions of NO and N_2O occur after rewetting dry soil. Accumulation of N compounds during soil drying, rewetting increased gas emissions due to chemical or biological reactions.
(Leitner, Minixhofer, et al., 2017)	NH_4^+, NO_3^- and amino acids	Temperate	Forest	Rosalia, Austria	5	Milli Q water	N	dry/rewet	Using MD technique, upon soil rewetting a detection of NO_3^- and some amino acids was visible, but in soil extractions with water no detection. MD much more sensible to detecting nutrient fluxes in soils.
(Oyewole et al., 2017)	NH_4^+, NO_3^- and amino acids	Boreal	Forest	Umeå/ Vindeln Sweden	1	Milli Q water Dextran	N	moist	First study on the potential mass flow has on N fluxes in 2 boreal forests. Amino acids dominated in the absence of mass flow, but in the presence of mass flow, NO_3^- was abundant.

(Ganeteg et al., 2017)	NH_4^+, NO_3^- and amino acids	Boreal	Agricultural	Umeå, Sweden	5	Milli Q water	Y	moist	The Lysine Histidine Transporter 1 (LHT1 - high-affinity transporter for both amino acids lysine and histidine) found in the genetically modified plant *Arabidopsis thaliana* is the first transporter that facilitates organic N uptake.
(Jämtgård et al., 2018)	Peptides	Boreal	Forest Agricultural	Umeå, Sweden	5	Milli Q water	Y/N	moist	First study sampling di- and tripeptides from soil solution using MD technique. Peptides and amino acids are similar in terms of diffusive properties - depletion over time, and dependent on molecular weight.
(Warren, 2018)	Alanine	Subtropical	Grassland	western Sydney, Australia	2	Milli Q water, artificial soil solution	N	moist	First coupling of MD to online organic N analysis via mass spectrometry. Soil microbes take up alanine much faster than plants making it undetectable after short period of time (5-20 min).
(Chin et al., 2018)	NH_4^+, NO_3^-	Subtropical	Waste	Queensland, Australia	5	Milli Q water	Y	moist	Three different sorption capacity sorbent amended organic wastes with different sorbent/waste ratio were used to measure diffusive fluxes of NH_4^+ and NO_3^- via MD method.
(Hill et al., 2019)	NH_4^+, NO_3^- and amino acids	Temperate	Grassland	Wales, UK	5	Milli Q water	Y	moist	Quantifying N compounds found in plant (clover) and soil fauna

									(earthworm) residues over the span of 6 days. Soil nutrient concentrations are several magnitudes higher closer to the roots than in bulk soil solution.
(Buckley et al., 2019)	Protein	Subtropical	Agricultural	Queenslan d, Australia	1	Milli Q water, Na-Aceta te	Y	moist	First study to investigate in situ soil enzyme activity using MD technique. MD is able to distinguish between free enzymes from soil solution and those bound to soil particles. Litter addition promotes free enzymes production by soil microbes as opposed to stabilized enzymes.
(Humphrey et al., 2019)	Iodine	Temperate	Forest Agricultural	Nottingha mshire, UK	5	Milli Q water	Y/N	moist	First study of MD soil sampling paired with ICP-MS on iodine species from soils and soil solution.
(Randewig et al., 2019)	Organic compounds	Boreal	Forest	Åheden, Sweden	5	Milli Q water	N	moist	First study to measure diffusive flux rates of low molecular weight organic compounds (LMWOC) using MD.
(Gao & DeLuca, 2019)	NH_4^+, NO_3^- and amino acids	Temperate	Forest	Montana, USA	5	Milli Q water	N	moist	Biochar was added at the surface or mixed through entire soil column. NO_3^- was more concentrated at the soil surface following biochar addition. For NH_4^+ and amino acids, biochar addition matched the vertical distribution of N compounds

									throughout the soil column no matter the addition approach.
(McKay Fletcher et al., 2019)	Phosphate	Temperate	Grassland	Wales, UK	3.3	Milli Q water Citrate	Y	moist	Root exudation of organic acids (citrate, oxalate) by plant roots aid in solubilization and bioavailability of phosphorus in soils. MD results concluded that citrate has no significant impact on the P uptake in soil.
(Clunes et al., 2020)	NO_2^-, NO_3^-, and NH_4^+	Temperate	Agricultural	southern Chile	5	Milli Q water	Y	rewet	First study on diffusive N fluxes measuring the impact of rewetting on soils derived from volcanic materials. The porous system is an important parameter to predict increases/decreases in N fluxes.
(Humphrey et al., 2020)	Iodine	Temperate	Agricultural	Nottinghamshire, UK	5	Milli Q water	Y	moist	Short-term monitoring of iodine indicates a rapid loss of I from solution. Iodine is either sorbed onto inorganic soil phases or immobilized by SOM.
(Schack-Kirchner et al., 2020)	Phosphate	Temperate	Forest	Northern Bavaria, Germany	3	citrate	N	moist	Microdialysis is a great tool to mobilize P from soil`s solid phase by using citrate as a perfusate.
(Petroselli et al., 2021)	Phosphate	Temperate	Grassland	Wales, UK	3.3	Milli Q water	N	moist	Microdialysis and X-ray CT to measure P transport in soil, a noninvasive detection over a period of time.
(Inselsbacher et	NH_4^+, NO_3^- and	Temperate	Agricultural	Lower Austria	5	Milli Q water	Y	moist	Abiotic and biotic factors influence diffusion of N

al., 2021)	amino acids								fluxes directly or indirectly through differences in production or consumption rates.
(Gao & DeLuca , 2021)	NH_4^+, NO_3^-, and ortho-P	Boreal	Forest	Montana, USA	5	Milli Q water	Y/N	moist	First study to assess the influence of wood pyrogenic carbon (PyC) and fire retardant on soil inorganic N and ortho-P fluxes. Wood PyC works as a buffer, modifying excess of nutrients induced by fire retardant applications.
(Maddala et al., 2021)	NH_4^+, NO_3^- and amino acids	Subtropical	Wetland	Cave Springs, Arkansas	2	Milli Q water	N	moist	Microdialysis technology turned out to be efficient in monitoring mineral N pulses in a riparian wetland soil.
(Hamilton et al., 2021)	Cr^{VI}	Temperate	Grassland	Glasgow UK, USA, Kenya Africa	3	Milli Q water	N	moist	First study on microdialysis coupled with HPLC-ICP-MS to investigate chromium VI in soil solution.
(Homyak et al., 2021)	NH_4^+, NO_3^- and amino acids	Arctic	Tundra	Toolik, USA	5	Milli Q water	N	moist	Amino acids rates were 3x higher than those of inorganic N in tussock tundra. Positively charged amino acids made up 68% of total amino acid N flux rate.
(Lim et al., 2021)	NH_4^+, NO_3^- and amino acids	Boreal	Forest	Umeå, Sweden	5	Milli Q water	Y/N	moist	Plant nutrition based on organic N may be a feasible alternative for decreasing N leaching, especially for plant species adapted to boreal regions where high soil acidity

									and lower temperatures inhibit N mineralization.
(Slessarev et al., 2021)	NO_2^-, NO_3^-, and NH_4^+	Subtropical	Grassland	California, USA	2	Milli Q water	N	dry	Nitric oxide (NO) emission is induced by 2 phases while soil wetting: (1) abiotic; driven by soil acidity at mineral surfaces; (2) prolonged pulse of emission by biological processes of NO_2^- and NH_3 oxidation. NO_2^- oxidizing microorganisms respond to wetting more slowly than NH_3 oxidizers.
(Heinzle et al., 2021)	NH_4^+, NO_3^- and amino acids	Temperate	Forest	Achenkirch, Austria	5	Milli Q water	N	moist	Diffusive fluxes of N remain unchanged after 14 years of artificial soil warming.
(Bailey et al., 2022)	NH_4^+, NO_3^- and amino acids	Subtropical	Agricultural	Queenslan d, Australia	5	Milli Q water	Y	moist	Delaying processing of soil samples show increase in N fluxes, (after 24 h refrigerated and 1 month refrigerated or air-dried) regardless of the sampling technique (conventional/microdialysis). In situ sampling or in-field extracts right after soil collection is preferred to get accurate plant-available N results.
(Smolander et al., 2022)	NH_4^+, NO_3^- and amino acids	Boreal	Forest	Sotkamo, Finland	5	Milli Q water	N	moist	Three levels of N fertilization over the span of 3 decades was analyzed to see the response in tree ring N (in particular isotope

									ratio $\delta^{15}N$) to repeated fertilizations. N availability was still high after the last fertilization, but tree diameter growth faded after a shorter period of time.
(Qiao et al., 2022)	Phenolic acid	Subtropical	Agricultural	Yuncheng, China	2	NaCl, adjusted by HCl	Y	moist	First MD-HPLC study on phenolic acids, sampling without changing the rhizosphere environment. Phenolic acid concentration increased close to roots.
(Buckley et al., 2022)	NO_2^-, NO_3^-, and NH_4^+	Boreal	Forest	Umeå, Sweden	1	Milli Q water, sucrose solution (0.5 or 5 mM)	N	moist	Two experiments were conducted with different concentrations of sucrose solutions (0.5 & 5 mM). Sucrose was used as a C source to investigate the influence on inorganic N. Because of accelerated microbial activity and increased N demand under C-rich circumstances, sucrose release did not result in an increase in inorganic N availability.
(Müller et al., 2023)	NH_4^+, NO_3^- and PO_4^{3-}	Temperate	Agricultural Grasslands	Vienna, Austria	1, 5, 10	Milli Q water	N	dry	First application of microdialysis in dry soils. The losses of perfusate amounts through leaching are decreased when high perfusion rate (10 µl min^{-1}) is used.

4. CONCLUSION

In this study, the influence of soil parameters on nutrient diffusion were assessed. A comprehensive analysis of the factors controlling nutrient supply via diffusion was presented. The interrelationships of each parameter related to and in connection with nutrient diffusion tend to be rather difficult to describe due to the soil`s natural complexity and the continuous changes occurring with each alteration in the soil systems. Each parameter has an important influence on nutrient availability, and as Fick`s law states, diffusivity, concentration gradient and path length are the main drivers of diffusion. All three processes are influenced by physical, chemical, and biological properties as mentioned in the third chapter and described further in this review. Source-sinks relations are of great importance for they increase or lower the concentration gradient that affect diffusion processes. They determine available nutrient concentration in soils and are proportional to diffusion fluxes of solutes. An understanding of source-sink relations can help improve the knowledge on nutrient diffusion in soils.

The main factors involved in the transport of water are considered most vital to help narrow down the most influential controls of nutrient diffusion. In ***Table 7*** can be found that from the existing literature on microdialysis studies of element fluxes, drying rewetting cycles increases N fluxes related to moist conditions. With this in mind, the presence of water in soils not only encourages chemical reactions but also more microbial processes happen in the presence of moisture. Equally important are the physical properties that shape the amount of water available with textural, structural differences that are known to indicate such changes. Together with biological properties, chemical controls aid in the movement of nutrients (Delgado & Gómez, 2016). Although other soil properties are affecting the chemical controls, the most influential is pH value, because acidic conditions restrict an optimal bacterial activity. In addition, cation exchange capacity might be equally important. There have been a lot of studies published on CEC stating that CEC levels are further affected by soil organic matter and soil textures. At the same time, AEC coupled with CEC, both influence pH levels either lowering the pH values with the addition of nutrient cations or on the contrary, with more anion uptake, exhibiting higher pH values (Kant & Kafkafi, 2013).

Biological activity, as De Nobili et al. (2002) highlights in his work, is considered to be a significant control in managing the organic and inorganic compounds in soil systems. The biological controls of soil presented in this study are closely bound together, each

influencing in different degrees and because of this they are important for nutrient availability along with soil nutrient supply via diffusion processes.

As mentioned at the beginning of this review, microdialysis technique can measure various compounds and the majority of papers published so far focus mainly on inorganic and organic N fluxes, first introduced by Inselsbacher et al. (2011). Other solute samplings include amino acids (peptides, alanine…), phosphates, iodine, protein, chromium 6 and others. ***Table 7*** encompasses all the existing microdialysis studies published so far, however due to time constraints and the scope of the thesis, only part of the gathered data is added in the table.

Moreover, some of the key interpretations from the multitude of articles are outlined briefly. Overall, the data gathered from all the articles concludes that there are no significant differences in diffusion rates between ammonium, nitrate, and free amino acids (FAA). However, it is shown that fertilization increases the overall N diffusion in soils, thus highlighting the source being an essential parameter for the concentration gradient. Oyewole et al. (2016) monitored N-fertilized and N limited soil diffusive fluxes using microdialysis at the onset of summer and the end of growing season in autumn. The results for NH_4^+ in the month of June for the fertilized soil were 69.2 nmol m^{-2} s^{-1} and 29.3 nmol m^{-2} s^{-1} for the control soil. In the month of September, the results for NH_4^+ were 13.36 nmol m^{-2} s^{-1} for the fertilized soil and 5.84 nmol m^{-2} s^{-1} for the control soil. The lower values suggest that the onset period is higher in N concentrations due to freezing/thaw cycles that influence N turnover (Oyewole et al., 2016). In another study conducted by Lim et al. (2021) it is underlined that organic fertilizer (arginine) yielded higher N concentrations and so it is preferred over inorganic fertilizer (ammonium nitrate). Additionally, the fluxes of N were lower in organic horizons as opposed to mineral horizons. This suggests that microbial activity is influencing the O horizons in the soil systems. The chemical element fluxes depicted from the publications decreased as is in the composition of soils and the Earth crust as follows: N, P, Iodine, Cd, Pb, Ni etc.

Until now, there is still much uncertainty about the controls of nutrient diffusion in soils. Considering that the present work is a review on existing literature, more research studies should be conducted at the field level to really understand the influence and the drivers of nutrient diffusion in soil systems. Some of the major drivers involved in nutrient diffusion should be addressed in future studies. Furthermore, the studies on microdialysis techniques should focus more on long-term analyses. Other potential experiments to analyze would include: sorption in comparison to microbial uptake effects on diffusive fluxes, the

tortuosity factor from microtomography technique (microCT) as a dependence on water filled pore space, the soils buffering capacity compared with total element content, CEC, AEC, microbial extracellular enzyme activity (EEA) and microbial activity.

Finally, measurements of other compounds not studied yet, such as alkali and earth alkali elements, would offer a different approach to sampling with microdialysis method, which have so far been analyzed only with ICP-MS. There are various new potential experiments that could focus on diffusion in particular including the majority of main controlling factors, that shape the movement of nutrients in soils. These should be taken into account in helping to understand the dynamics of diffusion in terrestrial systems.

Acknowledgments

I am forever thankful for the professional help and patience of Prof. Wolfgang Wanek and Prof. Erich Inselsbacher. Having such great mentors also helped me to get out of my comfort zone and improve my personal growth.

I want to express my deepest gratitude toward my friends, and boyfriend, who gave me the energy and motivation I needed in order to write this thesis. I cannot thank them enough for the advice and for lightening up my path to better understand and finally make this happen.

I want to thank my family for believing in me and cheering me up when I encountered obstacles. Thank you, everyone, I appreciate all the help as well as all the criticism that helped me grow.

REFERENCES

Adhya, T. K., Lal, B., Mohapatra, B., Paul, D., & Das, S. (2018). *Advances in soil microbiology: recent trends and future prospects*. Springer.

Agalakova, N., Lapin, A., & Gusev, G. (1997). Temperature effects on ion transport across the erythrocyte membrane of the frog Rana temporaria. *Comparative Biochemistry and Physiology Part A: Physiology, 117*(3), 411-418.

Amézketa, E. (1999, 1999/07/16). Soil Aggregate Stability: A Review. *Journal of Sustainable Agriculture, 14*(2-3), 83-151. https://doi.org/10.1300/J064v14n02_08

Amrute, A. P., Łodziana, Z., Schreyer, H., Weidenthaler, C., & Schüth, F. (2019). High-surface-area corundum by mechanochemically induced phase transformation of boehmite. *Science, 366*(6464), 485-489.

Annan, K. (2012). Mathematical modeling of the dynamic exchange of solutes during bicarbonate dialysis. *Mathematical and Computer Modelling, 55*(5-6), 1691-1704.

Azarbad, H., Niklińska, M., Laskowski, R., van Straalen, N. M., van Gestel, C. A. M., Zhou, J., He, Z., Wen, C., & Röling, W. F. M. (2014). Microbial community composition and functions are resilient to metal pollution along two forest soil gradients. *FEMS Microbiology Ecology, 91*(1), 1-11. https://doi.org/10.1093/femsec/fiu003

Bachmann, J., Guggenberger, G., Baumgartl, T., Ellerbrock, R. H., Urbanek, E., Goebel, M. O., Kaiser, K., Horn, R., & Fischer, W. R. (2008). Physical carbon-sequestration mechanisms under special consideration of soil wettability. *Journal of Plant Nutrition and Soil Science, 171*(1), 14-26.

Bailey, T., Robinson, N., Farrell, M., Macdonald, B., Weaver, T., Antille, D. L., Chin, A., & Brackin, R. (2022). Storage of soil samples leads to over-representation of the contribution of nitrate to plant-available nitrogen. *Soil Research, 60*(1), 22-32. https://doi.org/https://doi.org/10.1071/SR21013

Baldrian, P., Šnajdr, J., Merhautová, V., Dobiášová, P., Cajthaml, T., & Valášková, V. (2013). Responses of the extracellular enzyme activities in hardwood forest to soil temperature and seasonality and the potential effects of climate change. *Soil Biology and Biochemistry, 56*, 60-68.

Ball, J. (2001). Soil and water relationships.

Barber, S. A. (1995). *Soil nutrient bioavailability: a mechanistic approach*. John Wiley & Sons.

Barraclough, P., & Tinker, P. (1981). The determination of ionic diffusion coefficients in field soils. I. Diffusion coefficients in sieved soils in relation to water content and bulk density. *Journal of Soil Science, 32*(2), 225-236.

Barraclough, P., & Tinker, P. (1982). The determination of ionic diffusion coefficients in field soils. II. Diffusion of bromide ions in undisturbed soil cores. *Journal of Soil Science, 33*(1), 13-24.

Barrón, V., & Torrent, J. (2013, 01/01). Iron, manganese and aluminium oxides and oxyhydroxides. *European Mineralogical Union Notes in Mineralogy, 14*, 297-336. https://doi.org/10.1180/EMU-notes.14.9

Behroozi, A., Arora, M., Fletcher, T. D., Western, A. W., & Costelloe, J. F. (2021, 2021/06/01). Understanding the Impact of Soil Clay Mineralogy on the Adsorption Behavior of Zinc. *International Journal of Environmental Research, 15*(3), 559-569. https://doi.org/10.1007/s41742-021-00334-0

Bettermann, A., Zethof, J. H. T., Babin, D., Cammeraat, E. L. H., Solé-Benet, A., Lázaro, R., Luna, L., Nesme, J., Sørensen, S. J., Kalbitz, K., Smalla, K., & Vogel, C. (2021, 2021/08/01/). Importance of microbial communities at the root-soil interface for extracellular polymeric substances and soil aggregation in semiarid grasslands. *Soil Biology and Biochemistry, 159*, 108301. https://doi.org/https://doi.org/10.1016/j.soilbio.2021.108301

Bhadoria, P., Kaselowsky, J., Claassen, N., & Jungk, A. (1991). Soil phosphate diffusion coefficients: their dependence on phosphorus concentration and buffer power. *Soil Science Society of America Journal, 55*(1), 56-60.

Bian, H., Li, C., Zhu, J., Xu, L., Li, M., Zheng, S., & He, N. (2022). Soil moisture affects the rapid response of microbes to labile organic C addition. *Frontiers in Ecology and Evolution*, 604.

Bier, R. L., Bernhardt, E. S., Boot, C. M., Graham, E. B., Hall, E. K., Lennon, J. T., Nemergut, D. R., Osborne, B. B., Ruiz-González, C., Schimel, J. P., Waldrop, M. P., & Wallenstein, M. D. (2015). Linking microbial community structure and microbial processes: an empirical and conceptual overview. *FEMS Microbiology Ecology, 91*(10). https://doi.org/10.1093/femsec/fiv113

Bolan, N. S., Curtin, D., & Adriano, D. C. (2005). ACIDITY. In D. Hillel (Ed.), *Encyclopedia of Soils in the Environment* (pp. 11-17). Elsevier. https://doi.org/https://doi.org/10.1016/B0-12-348530-4/00173-9

Borggaard, O. (1983). Effect of surface area and mineralogy of iron oxides on their surface charge and anion-adsorption properties. *Clays and Clay Minerals, 31*(3), 230-232.

Borggaard, O. K., Szilas, C., Gimsing, A. L., & Rasmussen, L. H. (2004). Estimation of soil phosphate adsorption capacity by means of a pedotransfer function. *Geoderma, 118*(1-2), 55-61.

Bot, A., Benites, J., Food, & Nations, A. O. o. t. U. (2005). *The Importance of Soil Organic Matter: Key to Drought-resistant Soil and Sustained Food Production*. Food and Agriculture Organization of the United Nations. https://books.google.at/books?id=dJe5-pmmjaAC

Brackin, R., Atkinson, B. S., Sturrock, C. J., & Rasmussen, A. (2017, Dec). Roots-eye view: Using microdialysis and microCT to non-destructively map root nutrient depletion and accumulation zones. *Plant Cell Environ, 40*(12), 3135-3142. https://doi.org/10.1111/pce.13072

Brackin, R., Näsholm, T., Robinson, N., Guillou, S., Vinall, K., Buckley, S., Lakshmanan, P., Schmidt, S., & Inselsbacher, E. (2016). Microdialysis–a new technology for investigating soil nitrogen fluxes in the rhizosphere. 7th international nitrogen initiative conference,

Brackin, R., Näsholm, T., Robinson, N., Guillou, S., Vinall, K., Lakshmanan, P., Schmidt, S., & Inselsbacher, E. (2015). Nitrogen fluxes at the root-soil interface show a mismatch of nitrogen fertilizer supply and sugarcane root uptake capacity. *Scientific Reports, 5*(1), 1-9.

Briggs, G. G. (1981). Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor. *Journal of Agricultural and Food Chemistry, 29*(5), 1050-1059.

Bronick, C. J., & Lal, R. (2005). Soil structure and management: a review. *Geoderma, 124*(1-2), 3-22.

Buckley, S., Allen, D., Brackin, R., Jämtgård, S., Näsholm, T., & Schmidt, S. (2019). Microdialysis as an in situ technique for sampling soil enzymes. *Soil Biology and Biochemistry, 135*, 20-27. https://doi.org/10.1016/j.soilbio.2019.04.007

Buckley, S., Brackin, R., Jämtgård, S., Näsholm, T., & Schmidt, S. (2020). Microdialysis in soil environments: Current practice and future perspectives. *Soil Biology and Biochemistry, 143*. https://doi.org/10.1016/j.soilbio.2020.107743

Buckley, S., Brackin, R., Näsholm, T., Schmidt, S., & Jämtgård, S. (2017). Improving in situ recovery of soil nitrogen using the microdialysis technique. *Soil Biology and Biochemistry, 114*, 93-103. https://doi.org/10.1016/j.soilbio.2017.07.009

Buckley, S., Brackin, R., Näsholm, T., Schmidt, S., & Jämtgård, S. (2022). The influence of sucrose on soil nitrogen availability–A root exudate simulation using microdialysis. *Geoderma, 409*, 115645.

Burns, R. G., DeForest, J. L., Marxsen, J., Sinsabaugh, R. L., Stromberger, M. E., Wallenstein, M. D., Weintraub, M. N., & Zoppini, A. (2013). Soil enzymes in a changing environment: current knowledge and future directions. *Soil Biology and Biochemistry, 58*, 216-234.

Caldwell, B. A. (2005). Enzyme activities as a component of soil biodiversity: a review. *Pedobiologia, 49*(6), 637-644.

Cameron, K., & Buchan, G. (2006). Porosity and pore size distribution. *Encyclopedia of soil science, 2*, 1350-1353.

Chapin, F. S., Matson, P. A., & Vitousek, P. M. (2011). Plant nutrient use. In *Principles of terrestrial ecosystem ecology* (pp. 229-258). Springer.

Chen, G., Zhu, H., & Zhang, Y. (2003, 2003/07/01/). Soil microbial activities and carbon and nitrogen fixation. *Research in Microbiology, 154*(6), 393-398. https://doi.org/https://doi.org/10.1016/S0923-2508(03)00082-2

Chen, J., Zheng, Y., Guo, Y., Li, F., Xu, D., Chao, L., Qu, H., Wang, B., Ma, X., Wang, S., & Bao, Y. (2021). Differences in microbial communities from Quaternary volcanic soils at different stages of development: Evidence from Late Pleistocene and Holocene volcanoes. *Catena, 201*. https://doi.org/10.1016/j.catena.2021.105211

Chen, Y., Tessier, S., & Rouffignat, J. (1998). SOIL BULK DENSITY ESTIMATION FOR TILLAGE SYSTEMS AND SOIL TEXTURES. *Transactions of the ASAE, 41*(6), 1601-1610. https://doi.org/https://doi.org/10.13031/2013.17328

Chen, Z., Liu, H.-y., Rao, C., Jiang, C., Tan, Y.-c., Yu, T., Yu, E.-j., & Wu, P. (2021, 2021/05/01/). Soil microbial community dynamics indicate disruption of nitrogen cycling by pollution in vegetation buffer zones. *Pedobiologia, 85-86*, 150722. https://doi.org/https://doi.org/10.1016/j.pedobi.2021.150722

Chesworth, W. (2008). Encyclopedia of soil science.

Chin, A., Schmidt, S., Buckley, S., Pirie, R., Redding, M., Laycock, B., Luckman, P., Batstone, D., Robinson, N., & Brackin, R. (2018). Sorbents can tailor nitrogen

release from organic wastes to match the uptake capacity of crops. *Science of The Total Environment, 645*, 1474-1483.

Chorover, J., & Brusseau, M. L. (2008). Kinetics of Sorption—Desorption. In S. L. Brantley, J. D. Kubicki, & A. F. White (Eds.), *Kinetics of Water-Rock Interaction* (pp. 109-149). Springer New York. https://doi.org/10.1007/978-0-387-73563-4_4

Chou, H., Wu, L., Zeng, L., & Chang, A. (2012). Evaluation of solute diffusion tortuosity factor models for variously saturated soils. *Water Resources Research, 48*(10). https://doi.org/10.1029/2011wr011653

Clay and Clay Minerals. (2021). IntechOpen. https://doi.org/10.5772/intechopen.95640

Clunes, J., Deltedesco, E., Pinochet, D., Mentler, A., Inselsbacher, E., & Keiblinger, K. M. (2020). Inorganic Nitrogen diffusion in undisturbed volcanic soils during continuous drying–rewetting cycles. *Journal of Plant Nutrition and Soil Science, 183*(6), 648-658. https://doi.org/https://doi.org/10.1002/jpln.202000211

Cocovi-Solberg, D. J., Rosende, M., & Miró, M. (2014). Automatic kinetic bioaccessibility assay of lead in soil environments using flow-through microdialysis as a front end to electrothermal atomic absorption spectrometry. *Environmental Science & Technology, 48*(11), 6282-6290.

Comerford, N. (2005). Soil factors affecting nutrient bioavailability. In *Nutrient acquisition by plants* (pp. 1-14). Springer.

Conant, R. T., Ryan, M. G., Ågren, G. I., Birge, H. E., Davidson, E. A., Eliasson, P. E., Evans, S. E., Frey, S. D., Giardina, C. P., & Hopkins, F. M. (2011). Temperature and soil organic matter decomposition rates–synthesis of current knowledge and a way forward. *Global change biology, 17*(11), 3392-3404.

Conkling, B., & Blanchar, R. (1989). Calcium, magnesium, and potassium diffusion coefficients in soil estimated from electrical conductance. *Soil Science Society of America Journal, 53*(6), 1685-1690.

Crowther, T. W., Hoogen, J. v. d., Wan, J., Mayes, M. A., Keiser, A. D., Mo, L., Averill, C., & Maynard, D. S. (2019). The global soil community and its influence on biogeochemistry. *Science, 365*(6455), eaav0550. https://doi.org/doi:10.1126/science.aav0550

Dalal, R. C. (1998). Soil microbial biomass—what do the numbers really mean? *Australian Journal of Experimental Agriculture, 38*(7), 649-665. https://doi.org/https://doi.org/10.1071/EA97142

Darrah, P. (1991a). Measuring the diffusion coefficient of rhizosphere exudates in soil. I. The diffusion of non-sorbing compounds. *Journal of Soil Science, 42*(3), 413-420.

Darrah, P. (1991b). Measuring the diffusion coefficients or rhizosphere exudates in soil. II. The diffusion of sorbing compounds. *Journal of Soil Science, 42*(3), 421-434.

De Nobili, M., Francaviglia, R., & Sequi, P. (2002). Retention and mobility of chemicals in soil. In A. Violante, P. M. Huang, J. M. Bollag, & L. Gianfreda (Eds.), *Developments in Soil Science* (Vol. 28, pp. 171-196). Elsevier. https://doi.org/https://doi.org/10.1016/S0166-2481(02)80053-8

Delgado, A., & Gómez, J. A. (2016). The Soil. Physical, Chemical and Biological Properties. In F. J. Villalobos & E. Fereres (Eds.), *Principles of Agronomy for Sustainable Agriculture* (pp. 15-26). Springer International Publishing. https://doi.org/10.1007/978-3-319-46116-8_2

Demand, D., Schack-Kirchner, H., & Lang, F. (2017). Assessment of diffusive phosphate supply in soils by microdialysis. *Journal of Plant Nutrition and Soil Science, 180*(2), 220-230.

Deng, Q., Cheng, X., Hui, D., Zhang, Q., Li, M., & Zhang, Q. (2016, 2016/01/15/). Soil microbial community and its interaction with soil carbon and nitrogen dynamics following afforestation in central China. *Science of The Total Environment, 541*, 230-237. https://doi.org/https://doi.org/10.1016/j.scitotenv.2015.09.080

Diffusion coefficients in water. (n.d.). Retrieved from Hypertextbookshop.com: http://www.hypertextbookshop.com/biofilmbook/working_version/artifacts/tables/Module_004/Table4-1_DiffCoeffH2O.htm

Dorodnikov, M., Blagodatskaya, E., Blagodatsky, S., Marhan, S., Fangmeier, A., & Kuzyakov, Y. (2009). Stimulation of microbial extracellular enzyme activities by elevated CO2 depends on soil aggregate size. *Global change biology, 15*(6), 1603-1614.

Doucette, W. J. (2003). Quantitative structure-activity relationships for predicting soil-sediment sorption coefficients for organic chemicals. *Environmental Toxicology and Chemistry: An International Journal, 22*(8), 1771-1788.

DuPont, F. M. (1989). Effect of temperature on the plasma membrane and tonoplast ATPases of barley roots: comparison of results obtained with acridine orange and quinacrine. *Plant Physiology, 89*(4), 1401-1412.

Eash, N. S., Sauer, T. J., O'Dell, D., & Odoi, E. (2015). *Soil science simplified*. John Wiley & Sons.

Eusterhues, K., Neidhardt, J., Hädrich, A., Küsel, K., & Totsche, K. U. (2014, 2014/06/01). Biodegradation of ferrihydrite-associated organic matter. *Biogeochemistry, 119*(1), 45-50. https://doi.org/10.1007/s10533-013-9943-0

Foscolos, A. (1968). Cation-Exchange Equilibrium Constants of Aluminum-Saturated Montmorillonite and Vermiculite Clays. *Soil Science Society of America Journal, 32*(3), 350-354.

Foth, H. D. (1978). Fundamentals of soil science. *Soil Science, 125*(4), 272.

Fredriksson, M., & Thybring, E. E. (2018, 2018/08/01). Scanning or desorption isotherms? Characterising sorption hysteresis of wood. *Cellulose, 25*(8), 4477-4485. https://doi.org/10.1007/s10570-018-1898-9

Frey, S. D. (2007). 11 - SPATIAL DISTRIBUTION OF SOIL ORGANISMS. In E. A. Paul (Ed.), *Soil Microbiology, Ecology and Biochemistry (Third Edition)* (pp. 283-300). Academic Press. https://doi.org/https://doi.org/10.1016/B978-0-08-047514-1.50015-9

Frey, S. D. (2015). The spatial distribution of soil biota. *Soil microbiology, ecology, and biochemistry*, 223-244.

Fu, D., Wu, X., Duan, C., Smith, A. R., & Jones, D. L. (2020, 2020/06/15/). Traits of dominant species and soil properties co-regulate soil microbial communities across land restoration types in a subtropical plateau region of Southwest China. *Ecological Engineering, 153*, 105897. https://doi.org/https://doi.org/10.1016/j.ecoleng.2020.105897

Fujikawa, T., & Miyazaki, T. (2005). Effects of bulk density and soil type on the gas diffusion coefficient in repacked and undisturbed soils. *Soil Science, 170*(11), 892-901.

Ganeteg, U., Ahmad, I., Jämtgård, S., Aguetoni-Cambui, C., Inselsbacher, E., Svennerstam, H., Schmidt, S., & Näsholm, T. (2017). Amino acid transporter mutants of Arabidopsis provides evidence that a non-mycorrhizal plant acquires organic nitrogen from agricultural soil. *Plant, Cell & Environment, 40*(3), 413-423.

Gao, S., & DeLuca, T. H. (2019). Use of microdialysis to assess short-term soil soluble N dynamics with biochar additions. *Soil Biology and Biochemistry, 136*. https://doi.org/10.1016/j.soilbio.2019.06.008

Gao, S., & DeLuca, T. H. (2021, 2021/01/01). Influence of fire retardant and pyrogenic carbon on microscale changes in soil nitrogen and phosphorus. *Biogeochemistry, 152*(1), 117-126. https://doi.org/10.1007/s10533-020-00746-8

Gawlik, B., Sotiriou, N., Feicht, E., Schulte-Hostede, S., & Kettrup, A. (1997). Alternatives for the determination of the soil adsorption coefficient, KOC, of non-ionicorganic compounds—a review. *Chemosphere, 34*(12), 2525-2551.

German, D. P., Weintraub, M. N., Grandy, A. S., Lauber, C. L., Rinkes, Z. L., & Allison, S. D. (2011). Optimization of hydrolytic and oxidative enzyme methods for ecosystem studies. *Soil Biology and Biochemistry, 43*(7), 1387-1397.

Ghanbarian, B., Hunt, A. G., Ewing, R. P., & Sahimi, M. (2013). Tortuosity in porous media: a critical review. *Soil Science Society of America Journal, 77*(5), 1461-1477.

Glanville, H. C., Hill, P. W., Schnepf, A., Oburger, E., & Jones, D. L. (2016, 2016/03/01/). Combined use of empirical data and mathematical modelling to better estimate the microbial turnover of isotopically labelled carbon substrates in soil. *Soil Biology and Biochemistry, 94*, 154-168. https://doi.org/https://doi.org/10.1016/j.soilbio.2015.11.016

Gliński, J., & Lipiec, J. (2018). *Soil Physical Conditions and Plant Roots*. https://doi.org/10.1201/9781351076708

Goldberg, S. (2014). Application of surface complexation models to anion adsorption by natural materials. *Environmental Toxicology and Chemistry, 33*(10), 2172-2180.

Gougoulias, C., Clark, J. M., & Shaw, L. J. (2014). The role of soil microbes in the global carbon cycle: tracking the below-ground microbial processing of plant-derived carbon for manipulating carbon dynamics in agricultural systems. *Journal of the Science of Food and Agriculture, 94*(12), 2362-2371. https://doi.org/https://doi.org/10.1002/jsfa.6577

Griffiths, M., & York, L. M. (2020). Targeting Root Ion Uptake Kinetics to Increase Plant Productivity and Nutrient Use Efficiency1[OPEN]. *Plant Physiology, 182*(4), 1854-1868. https://doi.org/10.1104/pp.19.01496

Gruba, P., & Mulder, J. (2015, 2015/04/01/). Tree species affect cation exchange capacity (CEC) and cation binding properties of organic matter in acid forest soils. *Science of The Total Environment, 511*, 655-662. https://doi.org/https://doi.org/10.1016/j.scitotenv.2015.01.013

Hakeem, K. R., Akhtar, J., & Sabir, M. (2016). *Soil science: agricultural and environmental prospectives*. Springer.

Hamilton, E. M., Young, S. D., Bailey, E. H., Humphrey, O. S., & Watts, M. J. (2021, 2021/02/16). Online Microdialysis-High-Performance Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry (MD-HPLC-ICP-MS) as a Novel Tool for Sampling Hexavalent Chromium in Soil Solution. *Environmental Science & Technology, 55*(4), 2422-2429. https://doi.org/10.1021/acs.est.0c08140

Hartemink, A. E. (2016). Scheffer/Schachtschabel Soil Science. H.-P. Blume, GW Brümmer, H. Fleige, R. Horn, E. Kandeler, I. Kögel-Knabner, R. Kretzschmar, K. Stahr, B.-M. Wilke Springer, Dordrecht. 2016. 618 pp. $119. ISBN 978-3-642-30942-7.

Hartman, W. H., & Richardson, C. J. (2013). Differential nutrient limitation of soil microbial biomass and metabolic quotients (q CO2): is there a biological stoichiometry of soil microbes? *PloS one, 8*(3), e57127.

Hartmann, A., Gräsle, W., & Horn, R. (1998, 1998/06/02/). Cation exchange processes in structured soils at various hydraulic properties. *Soil and Tillage Research, 47*(1), 67-72. https://doi.org/https://doi.org/10.1016/S0167-1987(98)00074-9

Havlin, J. L. (2013). Fertility☆. In *Reference Module in Earth Systems and Environmental Sciences*. Elsevier. https://doi.org/https://doi.org/10.1016/B978-0-12-409548-9.05162-9

He, Y., Gu, F., Xu, C., & Chen, J. (2019). Influence of iron/aluminum oxides and aggregates on plant available water with different amendments in red soils. *Journal of Soil and Water Conservation, 74*(2), 145-159.

He, Z., Zhang, M., & Wilson, M. J. (2004). Distribution and Classification of Red Soils in China. In M. J. Wilson, Z. He, & X. Yang (Eds.), *The Red Soils of China: Their Nature, Management and Utilization* (pp. 29-33). Springer Netherlands. https://doi.org/10.1007/978-1-4020-2138-1_3

Hees, P., Jones, D., Finlay, R., Godbold, D., & Lundström, U. (2005, 01/31). The carbon we do not see - The impact of low molecular weight compounds on carbon dynamics and respiration in forest soils: A review. *Soil Biology and Biochemistry, 37*, 1-13. https://doi.org/10.1016/j.soilbio.2004.06.010

Heinzle, J., Wanek, W., Tian, Y., Kengdo, S. K., Borken, W., Schindlbacher, A., & Inselsbacher, E. (2021). No effect of long-term soil warming on diffusive soil inorganic and organic nitrogen fluxes in a temperate forest soil. *Soil Biology and Biochemistry, 158*, 108261.

Helliwell, J. R., Sturrock, C. J., Mairhofer, S., Craigon, J., Ashton, R. W., Miller, A. J., Whalley, W. R., & Mooney, S. J. (2017, 2017/11/01). The emergent rhizosphere: imaging the development of the porous architecture at the root-soil interface. *Scientific Reports, 7*(1), 14875. https://doi.org/10.1038/s41598-017-14904-w

Henderson, G. S. (1995). Soil Organic Matter: A Link Between Forest Management and Productivity. In *Carbon Forms and Functions in Forest Soils* (pp. 419-435). https://doi.org/https://doi.org/10.2136/1995.carbonforms.c19

Hill, D. (1984). Diffusion coefficients of nitrate, chloride, sulphate and water in cracked and uncracked Chalk. *Journal of Soil Science, 35*(1), 27-33.

Hill, E. J., Jones, D. L., Paterson, E., & Hill, P. W. (2019). Hotspots and hot moments of amino acid N in soil: Real-time insights using continuous microdialysis sampling. *Soil Biology and Biochemistry, 131*, 40-43. https://doi.org/10.1016/j.soilbio.2018.12.026

Holland, E. A., Neff, J. C., Townsend, A. R., & McKeown, B. (2000). Uncertainties in the temperature sensitivity of decomposition in tropical and subtropical ecosystems: implications for models. *Global Biogeochemical Cycles, 14*(4), 1137-1151.

Homyak, P. M., Slessarev, E. W., Hagerty, S., Greene, A. C., Marchus, K., Dowdy, K., Iverson, S., & Schimel, J. P. (2021). Amino acids dominate diffusive nitrogen fluxes across soil depths in acidic tussock tundra. *New Phytologist, 231*(6), 2162-2173.

Horwath, W. R., & Paul, E. A. (1994). Microbial Biomass. In *Methods of Soil Analysis* (pp. 753-773). https://doi.org/https://doi.org/10.2136/sssabookser5.2.c36

Hu, Y., Zheng, Q., Noll, L., Zhang, S., & Wanek, W. (2020, 2020/02/01/). Direct measurement of the in situ decomposition of microbial-derived soil organic matter. *Soil Biology and Biochemistry, 141*, 107660. https://doi.org/https://doi.org/10.1016/j.soilbio.2019.107660

Humphrey, O. S., Young, S. D., Bailey, E. H., Crout, N. M. J., Ander, E. L., Hamilton, E. M., & Watts, M. J. (2019, Aug). Investigating the use of microdialysis and SEC-UV-ICP-MS to assess iodine interactions in soil solution. *Chemosphere, 229*, 41-50. https://doi.org/10.1016/j.chemosphere.2019.04.215

Humphrey, O. S., Young, S. D., Crout, N. M. J., Bailey, E. H., Ander, E. L., & Watts, M. J. (2020, 2020/02/04). Short-Term Iodine Dynamics in Soil Solution. *Environmental Science & Technology, 54*(3), 1443-1450. https://doi.org/10.1021/acs.est.9b02296

Huuskonen, J. (2003). Prediction of soil sorption coefficient of a diverse set of organic chemicals from molecular structure. *Journal of chemical information and computer sciences, 43*(5), 1457-1462.

Inselsbacher, E., & Näsholm, T. (2012a). The below-ground perspective of forest plants: soil provides mainly organic nitrogen for plants and mycorrhizal fungi. *New Phytologist, 195*(2), 329-334.

Inselsbacher, E., & Näsholm, T. (2012b, 2012/05/01). A novel method to measure the effect of temperature on diffusion of plant-available nitrogen in soil. *Plant and Soil, 354*(1), 251-257. https://doi.org/10.1007/s11104-011-1061-y

Inselsbacher, E., Öhlund, J., Jämtgård, S., Huss-Danell, K., & Näsholm, T. (2011). The potential of microdialysis to monitor organic and inorganic nitrogen compounds in soil. *Soil Biology and Biochemistry, 43*(6), 1321-1332.

Inselsbacher, E., Oyewole, O. A., & Näsholm, T. (2014). Early season dynamics of soil nitrogen fluxes in fertilized and unfertilized boreal forests. *Soil Biology and Biochemistry, 74*, 167-176. https://doi.org/10.1016/j.soilbio.2014.03.012

Inselsbacher, E., Peticzka, R., & Dickinson, N. (2021). Diffusive fluxes and water-extractable concentrations of different nitrogen forms in a temperate agricultural soil. *Soil Research, 59*(8), 848-853.

Jagadamma, S., Mayes, M. A., & Phillips, J. R. (2012). Selective sorption of dissolved organic carbon compounds by temperate soils. *PloS one, 7*(11), e50434.

Jämtgård, S., Robinson, N., Moritz, T., Colgrave, M. L., & Schmidt, S. (2018). Optimising methods for the recovery and quantification of di-and tripeptides in soil. *Soil Research, 56*(4), 404-412.

Jiang, J., Wang, Y.-P., Yu, M., Cao, N., & Yan, J. (2018, 2018/11/30/). Soil organic matter is important for acid buffering and reducing aluminum leaching from acidic forest soils. *Chemical Geology, 501*, 86-94. https://doi.org/https://doi.org/10.1016/j.chemgeo.2018.10.009

Jiang, X., Shi, X., & Wright, A. L. (2013, 2013/05/01/). Seasonal variability of microbial biomass associated with aggregates in a rice-based ecosystem. *European Journal of Soil Biology, 56*, 84-88. https://doi.org/https://doi.org/10.1016/j.ejsobi.2013.03.004

Johnston, A., & Karamanos, R. (2005). Base saturation and basic cation saturation ratios–How do they fit in northern Great Plains soil analysis. *News & views. PPI & PPIC*.

Jones Jr, J. B. (2012). *Plant nutrition and soil fertility manual*. CRC press.

Kang, B., Tang, H., Zhao, Z., & Song, S. (2020). Hofmeister series: Insights of ion specificity from amphiphilic assembly and interface property. *ACS omega, 5*(12), 6229-6239.

Kant, S., & Kafkafi, U. (2013). Fertigation☆. In *Reference Module in Earth Systems and Environmental Sciences*. Elsevier. https://doi.org/https://doi.org/10.1016/B978-0-12-409548-9.05161-7

Kome, G. K., Enang, R. K., Tabi, F. O., & Yerima, B. P. K. (2019). Influence of clay minerals on some soil fertility attributes: a review. *Open Journal of Soil Science, 9*(9), 155-188.

Kumari, N., & Mohan, C. (2021). Basics of clay minerals and their characteristic properties. *Clay Clay Miner, 24*, 1-29.

Kuzyakov, Y., & Xu, X. (2013). Competition between roots and microorganisms for nitrogen: mechanisms and ecological relevance. *New Phytologist, 198*(3), 656-669.

Lambers, H., Chapin Iii, F. S., & Pons, T. (2008). *Plant Physiological Ecology, second edition* (Vol. 80). https://doi.org/10.2307/176572

LeFevre, G. H., Hozalski, R. M., & Novak, P. J. (2013). Root exudate enhanced contaminant desorption: an abiotic contribution to the rhizosphere effect. *Environmental Science & Technology, 47*(20), 11545-11553.

Leitner, S., Homyak, P. M., Blankinship, J. C., Eberwein, J., Jenerette, G. D., Zechmeister-Boltenstern, S., & Schimel, J. P. (2017). Linking NO and N2O emission pulses with the mobilization of mineral and organic N upon rewetting dry soils. *Soil Biology and Biochemistry, 115*, 461-466.

Leitner, S., Minixhofer, P., Inselsbacher, E., Keiblinger, K. M., Zimmermann, M., & Zechmeister-Boltenstern, S. (2017). Short-term soil mineral and organic nitrogen fluxes during moderate and severe drying–rewetting events. *Applied Soil Ecology, 114*, 28-33. https://doi.org/10.1016/j.apsoil.2017.02.014

Li, G. L., Zhou, C. H., Fiore, S., & Yu, W. H. (2019, 2019/09/01/). Interactions between microorganisms and clay minerals: New insights and broader applications. *Applied*

Clay Science, 177, 91-113. https://doi.org/https://doi.org/10.1016/j.clay.2019.04.025

Lim, H., Jämtgård, S., Oren, R., Gruffman, L., Kunz, S., & Näsholm, T. (2021). Organic nitrogen enhances nitrogen nutrition and early growth of Pinus sylvestris seedlings. *Tree Physiology, 42*(3), 513-522. https://doi.org/10.1093/treephys/tpab127

Loladze, I. (2002). Rising atmospheric CO2 and human nutrition: toward globally imbalanced plant stoichiometry? *Trends in Ecology & Evolution, 17*(10), 457-461.

Lu, J., Li, S., Liang, G., Wu, X., Zhang, Q., Gao, C., Li, J., Jin, D., Zheng, F., Zhang, M., Abdelrhman, A., & Degre, A. (2021). *The Contribution of Microorganisms to Soil Organic Carbon Stock Under Fertilization Varies among Aggregate Size Classes*. https://doi.org/10.21203/rs.3.rs-140931/v1

Luan, H., Yuan, S., Gao, W., Tang, J., Li, R., Zhang, H., & Huang, S. (2021). Aggregate-related changes in living microbial biomass and microbial necromass associated with different fertilization patterns of greenhouse vegetable soils. *European Journal of Soil Biology, 103*. https://doi.org/10.1016/j.ejsobi.2021.103291

Luo, L., Meng, H., & Gu, J.-D. (2017). Microbial extracellular enzymes in biogeochemical cycling of ecosystems. *Journal of Environmental Management, 197*, 539-549.

Maddala, S., Savin, M. C., Stenken, J. A., & Wood, L. S. (2021, 2021/05/20). Nitrogen Dynamics: Quantifying and Differentiating Fluxes in a Riparian Wetland Soil. *ACS Earth and Space Chemistry, 5*(5), 1254-1264. https://doi.org/10.1021/acsearthspacechem.0c00301

Malik, A. A., Puissant, J., Buckeridge, K. M., Goodall, T., Jehmlich, N., Chowdhury, S., Gweon, H. S., Peyton, J. M., Mason, K. E., van Agtmaal, M., Blaud, A., Clark, I. M., Whitaker, J., Pywell, R. F., Ostle, N., Gleixner, G., & Griffiths, R. I. (2018, 2018/09/04). Land use driven change in soil pH affects microbial carbon cycling processes. *Nature Communications, 9*(1), 3591. https://doi.org/10.1038/s41467-018-05980-1

Manzoni, S., Moyano, F., Kätterer, T., & Schimel, J. (2016, 2016/04/01/). Modeling coupled enzymatic and solute transport controls on decomposition in drying soils. *Soil Biology and Biochemistry, 95*, 275-287. https://doi.org/https://doi.org/10.1016/j.soilbio.2016.01.006

Manzoni, S., Trofymow, J. A., Jackson, R. B., & Porporato, A. (2010). Stoichiometric controls on carbon, nitrogen, and phosphorus dynamics in decomposing litter. *Ecological monographs, 80*(1), 89-106.

Marshall, T., Holmes, J., & Busscher, W. (1980). Soil Physics. 1979. *Soil Science, 130*(5), 293.

McGrath, J. M., & Lobell, D. B. (2013, Mar). Reduction of transpiration and altered nutrient allocation contribute to nutrient decline of crops grown in elevated CO(2) concentrations. *Plant Cell Environ, 36*(3), 697-705. https://doi.org/10.1111/pce.12007

McKay Fletcher, D. M., Shaw, R., Sánchez-Rodríguez, A. R., Daly, K. R., van Veelen, A., Jones, D. L., & Roose, T. (2019). Quantifying citrate-enhanced phosphate root uptake using microdialysis. *Plant and Soil*. https://doi.org/10.1007/s11104-019-04376-4

McKenzie, N., Jacquier, D., Isbell, R., & Brown, K. (2004). *Australian Soils and Landscapes: An Illustrated Compendium*. https://doi.org/10.1071/9780643100732

Meetei, T. T., Devi, Y., & Chanu, T. (2020, 05/04). Ion Exchange: The Most Important Chemical Reaction on Earth after Photosynthesis. *International Research Journal of Pure and Applied Chemistry, 21*, 31-42. https://doi.org/10.9734/IRJPAC/2020/v21i630174

Merrington, G., Fishwick, S., Barraclough, D., Morris, J., Preedy, N., Boucard, T., Reeve, M., Smith, P., & Fang, C. (2006). *The development and use of soil quality indicators for assessing the role of soil in environmental interactions*. Environment Agency.

Miró, M., Fitz, W. J., Swoboda, S., & Wenzel, W. W. (2010). In-situ sampling of soil pore water: evaluation of linear-type microdialysis probes and suction cups at varied moisture contents. *Environmental Chemistry, 7*(1), 123-131.

Miró, M., & Frenzel, W. (2003). A novel flow-through microdialysis separation unit with integrated differential potentiometric detection for the determination of chloride in soil samples. *Analyst, 128*(10), 1291-1297.

Miró, M., & Frenzel, W. (2004). Implantable flow-through capillary-type microdialyzers for continuous in situ monitoring of environmentally relevant parameters. *Analytical chemistry, 76*(19), 5974-5981.

Miró, M., Jimoh, M., & Frenzel, W. (2005). A novel dynamic approach for automatic microsampling and continuous monitoring of metal ion release from soils exploiting a dedicated flow-through microdialyser. *Analytical and bioanalytical chemistry, 382*(2), 396-404.

Mishra, G., Sulieman, M. M., Kaya, F., Francaviglia, R., Keshavarzi, A., Bakhshandeh, E., Loum, M., Jangir, A., Ahmed, I., & Elmobarak, A. (2022). Machine learning for cation exchange capacity prediction in different land uses. *Catena, 216*, 106404.

Moldrup, P., Olesen, T., Komatsu, T., Schjønning, P., & Rolston, D. (2001). Tortuosity, diffusivity, and permeability in the soil liquid and gaseous phases. *Soil Science Society of America Journal, 65*(3), 613-623.

Morris, S. J., & Blackwood, C. B. (2015). The ecology of the soil biota and their function. *Soil microbiology, ecology and biochemistry*, 273-309.

Müller, R., Peticzka, R., & Inselsbacher, E. (2023). Applicability of the microdialysis technique in dry soils: Impact of soil water content depends on perfusion flow rate. *Soil Biology and Biochemistry, 177*, 108903.

Ng, J. F., Ahmed, O., Jalloh, M. B., Omar, L., Kwan, Y., Musah, A., & Poong, K. (2022, 01/17). Soil Nutrient Retention and pH Buffering Capacity Are Enhanced by Calciprill and Sodium Silicate. *Agronomy, 12*, 219. https://doi.org/10.3390/agronomy12010219

Nimmo, J. R. (2004). Porosity and pore size distribution. *Encyclopedia of Soils in the Environment, 3*(1), 295-303.

Nunes, V. L. N., & Mulvaney, R. L. (2021, 2021/01/02). Rapid Saturation–Diffusion Method to Determine Cation- and Anion-Exchange Capacities in Soil. *Communications in Soil Science and Plant Analysis, 52*(1), 76-91. https://doi.org/10.1080/00103624.2020.1849264

Oldfield, E. E., Bradford, M. A., & Wood, S. A. (2019). Global meta-analysis of the relationship between soil organic matter and crop yields. *Soil, 5*(1), 15-32.

Olesen, T., Moldrup, P., & Gamst, J. (1999). Solute diffusion and adsorption in six soils along a soil texture gradient. *Soil Science Society of America Journal, 63*(3), 519-524.

Oliveira, E. M. M., Ruiz, H. A., Alvarez V, V. H., Ferreira, P. A., Costa, F. O., & Almeida, I. C. C. (2010). Nutrient supply by mass flow and diffusion to maize plants in response to soil aggregate size and water potential. *Revista Brasileira de Ciência do Solo, 34*, 317-328. http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-06832010000200005&nrm=iso

Osman, K. (2013). Organic Matter of Forest Soils. In (pp. 63-76). https://doi.org/10.1007/978-3-319-02541-4_4

Oyewole, O. A., Inselsbacher, E., & Näsholm, T. (2014, Feb). Direct estimation of mass flow and diffusion of nitrogen compounds in solution and soil. *New Phytol, 201*(3), 1056-1064. https://doi.org/10.1111/nph.12553

Oyewole, O. A., Inselsbacher, E., Näsholm, T., & Jämtgård, S. (2017). Incorporating mass flow strongly promotes N flux rates in boreal forest soils. *Soil Biology and Biochemistry, 114*, 263-269. https://doi.org/10.1016/j.soilbio.2017.07.021

Oyewole, O. A., Jämtgård, S., Gruffman, L., Inselsbacher, E., & Näsholm, T. (2016). Soil diffusive fluxes constitute the bottleneck to tree nitrogen nutrition in a Scots pine forest. *Plant and Soil, 399*(1), 109-120.

Pansu, M., & Gautheyrou, J. (2006). Anion Exchange Capacity. In. https://doi.org/10.1007/978-3-540-31211-6_27

Pennell, K. (2016). Specific Surface Area. In. https://doi.org/10.1016/B978-0-12-409548-9.09583-X

Petroselli, C., Williams, K. A., Ghosh, A., McKay Fletcher, D., Ruiz, S. A., Gerheim Souza Dias, T., Scotson, C. P., & Roose, T. (2021). Space and time-resolved monitoring of phosphorus release from a fertilizer pellet and its mobility in soil using microdialysis and X-ray computed tomography. *Soil Science Society of America Journal, 85*(1), 172-183.

Picariello, E., Baldantoni, D., Izzo, F., Langella, A., & De Nicola, F. (2021, 2021/06/01/). Soil organic matter stability and microbial community in relation to different plant cover: A focus on forests characterizing Mediterranean area. *Applied Soil Ecology, 162*, 103897. https://doi.org/https://doi.org/10.1016/j.apsoil.2021.103897

Prescott, C. E. (2005). Decomposition and Mineralization of Nutrients from Litter and Humus. In H. BassiriRad (Ed.), *Nutrient Acquisition by Plants: An Ecological Perspective* (pp. 15-41). Springer Berlin Heidelberg. https://doi.org/10.1007/3-540-27675-0_2

Qiao, B., Li, C., Liang, C., Li, X., Tian, M., Li, Q., Zhao, C., & Fu, Y. (2022). Determination of phenolic acids in Rehmannia glutinosa rhizosphere using a new method of microdialysis-HPLC. *South African Journal of Botany, 148*, 387-395.

Randewig, D., Marshall, J. D., Näsholm, T., & Jämtgård, S. (2019). Combining microdialysis with metabolomics to characterize the in situ composition of dissolved organic compounds in boreal forest soil. *Soil Biology and Biochemistry, 136*. https://doi.org/10.1016/j.soilbio.2019.107530

Rattan, R. K., & Deb, D. L. (1981, 1981/10/01). Self-diffusion of zinc and iron in soils as affected by pH, CaCO3, moisture, carrier and phosphorus levels. *Plant and Soil, 63*(3), 377-393. https://doi.org/10.1007/BF02370038

Reddy, P. (2016). Soil Organic Matter. In (pp. 157-173). https://doi.org/10.1007/978-981-10-2702-4_11

Rosende, M., Magalhães, L. M., Segundo, M. A., & Miró, M. (2013). Automated microdialysis-based system for in situ microsampling and investigation of lead bioavailability in terrestrial environments under physiologically based extraction conditions. *Environmental Science & Technology, 47*(20), 11668-11675.

Rothstein, D. E. (2010). Effects of amino-acid chemistry and soil properties on the behavior of free amino acids in acidic forest soils. *Soil Biology and Biochemistry, 42*(10), 1743-1750.

Roy, R. N., Finck, A., Blair, G., & Tandon, H. (2006). Plant nutrition for food security. *A guide for integrated nutrient management. FAO Fertilizer and Plant Nutrition Bulletin, 16*, 368.

Sabljić, A., Güsten, H., Verhaar, H., & Hermens, J. (1995). QSAR modelling of soil sorption. Improvements and systematics of log Koc vs. log Kow correlations. *Chemosphere, 31*(11-12), 4489-4514.

Schack-Kirchner, H., Loew, C. A., & Lang, F. (2020). The cumulative amount of exuded citrate controls its efficiency to mobilize soil phosphorus. *Frontiers in Forests and Global Change, 3*, 550884.

Schavemaker, P. E., Boersma, A. J., & Poolman, B. (2018). How important is protein diffusion in prokaryotes? *Frontiers in Molecular Biosciences, 5*, 93.

Scheinost, A., & Schwertmann, U. (1995). Predicting phosphate adsorption-desorption in a soilscape. *Soil Science Society of America Journal, 59*(6), 1575-1580.

Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D. A. C., Nannipieri, P., Rasse, D. P., Weiner, S., & Trumbore, S. E. (2011, 2011/10/01). Persistence of soil organic matter as an ecosystem property. *Nature, 478*(7367), 49-56. https://doi.org/10.1038/nature10386

Shaw, R., Williams, A., & Jones, D. (2014). Assessing soil nitrogen availability using microdialysis-derived diffusive flux measurements. *Soil Science Society of America Journal, 78*(5), 1797-1803.

Slessarev, E. W., Greene, A. C., Homyak, P. M., Ying, S. C., & Schimel, J. P. (2021). High resolution measurements reveal abiotic and biotic mechanisms of elevated nitric oxide emission after wetting dry soil. *Soil Biology and Biochemistry, 160*, 108316.

Smethurst, P. J. (2000). Soil solution and other soil analyses as indicators of nutrient supply: a review. *Forest Ecology and Management, 138*(1-3), 397-411.

Smith, S. E., Dickson, S., & Smith, F. A. (2001). Nutrient transfer in arbuscular mycorrhizas: how are fungal and plant processes integrated? *Functional Plant Biology, 28*(7), 685-696.

Smolander, A., Henttonen, H. M., Nöjd, P., Soronen, P., & Mäkinen, H. (2022, 2022/06/01). Long-term response of soil and stem wood properties to repeated nitrogen fertilization in a N-limited Scots pine stand. *European Journal of Forest Research, 141*(3), 421-431. https://doi.org/10.1007/s10342-022-01448-6

Sokołowska, Z. (2011). Specific surface area of soils and plants. *Encyclopedia of agrophysics*, 839-844.

Staunton, S. (2008). Diffusion Processes. In W. Chesworth (Ed.), *Encyclopedia of soil science* (pp. 185-191). Springer Netherlands. https://doi.org/10.1007/978-1-4020-3995-9_158

Strawn, D. G. (2021). Sorption mechanisms of chemicals in soils. *Soil Systems, 5*(1), 13.

Sulyok, M., Miro, M., Stingeder, G., & Koellensperger, G. (2005, Aug 1). The potential of flow-through microdialysis for probing low-molecular weight organic anions in rhizosphere soil solution. *Anal Chim Acta, 546*(1), 1-10. https://doi.org/10.1016/j.aca.2005.05.027

Svanidze, A. V., Koludarov, I. P., Lushnikov, S. G., Asenbaum, A., Pruner, C., Aliev, F. M., Chang, C.-C., & Kan, L.-s. (2012). Specific features of the temperature behavior of lysozyme diffusivity in solutions with different protein concentrations. *Journal of Molecular Liquids, 168*, 7-11.

Table of Diffusion coefficients. (2020). Retrieved from Aqion: https://www.aqion.de/site/diffusion-coefficients

Tertre, E., Savoye, S., Hubert, F., Prêt, D., Dabat, T., & Ferrage, E. (2018, 2018/02/20). Diffusion of Water through the Dual-Porosity Swelling Clay Mineral Vermiculite. *Environmental Science & Technology, 52*(4), 1899-1907. https://doi.org/10.1021/acs.est.7b05343

Tinker, P. B., & Nye, P. H. (2000). *Solute movement in the rhizosphere*. Oxford University Press.

Umar, W., Czinkota, I., Gulyás, M., Aziz, T., & Hameed, M. K. (2022). Development and characterization of slow release N and Zn fertilizer by coating urea with Zn fortified nano-bentonite and ZnO NPs using various binders. *Environmental Technology & Innovation, 26*, 102250.

Van Rees, K. C. J., Comerford, N. B., & Rao, P. S. C. (1990). Defining Soil Buffer Power: Implications for Ion Diffusion and Nutrient Uptake Modeling. *Soil Science Society of America Journal, 54*(5), 1505-1507. https://doi.org/https://doi.org/10.2136/sssaj1990.03615995005400050050x

Van Vuuren, M. M. I., Robinson, D., Fitter, A. H., Chasalow, S. D., Williamson, L., & Raven, J. A. (1997). Effects of elevated atmospheric CO2 and soil water availability on root biomass, root length, and N, P and K uptake by wheat. *New Phytologist, 135*(3), 455-465. https://doi.org/10.1046/j.1469-8137.1997.00682.x

Wang, L., & D'Odorico, P. (2013). Decomposition and Mineralization. In. https://doi.org/10.1016/B978-0-12-409548-9.00688-6

Wang, Q., Zhu, C., Yun, J., & Yang, G. (2017, 2017/12/07). Isomorphic Substitutions in Clay Materials and Adsorption of Metal Ions onto External Surfaces: A DFT Investigation. *The Journal of Physical Chemistry C, 121*(48), 26722-26732. https://doi.org/10.1021/acs.jpcc.7b03488

Wardle, D. A., Yeates, G. W., Nicholson, K. S., Bonner, K. I., & Watson, R. N. (1999, 1999/10/01/). Response of soil microbial biomass dynamics, activity and plant litter decomposition to agricultural intensification over a seven-year period. *Soil Biology and Biochemistry, 31*(12), 1707-1720. https://doi.org/https://doi.org/10.1016/S0038-0717(99)00090-5

Warncke, D., & Barber, S. (1972a). Diffusion of zinc in soil: I. The influence of soil moisture. *Soil Science Society of America Journal, 36*(1), 39-42.

Warncke, D., & Barber, S. (1972b). Diffusion of zinc in soil: II. The influence of soil bulk density and its interaction with soil moisture. *Soil Science Society of America Journal, 36*(1), 42-46.

Warren, C. R. (2018). Development of online microdialysis-mass spectrometry for continuous minimally invasive measurement of soil solution dynamics. *Soil Biology and Biochemistry, 123*, 266-275. https://doi.org/10.1016/j.soilbio.2018.05.022

Wei, H., Guenet, B., Vicca, S., Nunan, N., Asard, H., AbdElgawad, H., Shen, W., & Janssens, I. A. (2014, 2014/10/01/). High clay content accelerates the decomposition of fresh organic matter in artificial soils. *Soil Biology and Biochemistry, 77*, 100-108. https://doi.org/https://doi.org/10.1016/j.soilbio.2014.06.006

Winget, P., Cramer, C. J., & Truhlar, D. G. (2000). Prediction of soil sorption coefficients using a universal solvation model. *Environmental Science & Technology, 34*(22), 4733-4740.

Wikipedia contributors. (2023, January 26). Fertilizer. Retrieved from Wikipedia, The Free Encyclopedia: https://en.wikipedia.org/w/index.php?title=Fertilizer&oldid=1135690930

Xiao, E., Ning, Z., Xiao, T., Sun, W., & Jiang, S. (2021, 2021/06/01/). Soil bacterial community functions and distribution after mining disturbance. *Soil Biology and Biochemistry, 157*, 108232. https://doi.org/https://doi.org/10.1016/j.soilbio.2021.108232

Xu, X., Hui, D., King, A. W., Song, X., Thornton, P. E., & Zhang, L. (2015). Convergence of microbial assimilations of soil carbon, nitrogen, phosphorus and sulfur in terrestrial ecosystems. *Scientific Reports, 5*(1), 1-8.

Xu, X., Thornton, P. E., & Post, W. M. (2013). A global analysis of soil microbial biomass carbon, nitrogen and phosphorus in terrestrial ecosystems. *Global Ecology and Biogeography, 22*(6), 737-749. https://doi.org/https://doi.org/10.1111/geb.12029

Yan, M., Li, T., Li, X., Liu, Y., & Zhang, J. (2021). Microbial biomass and activity restrict soil function recovery of a post-mining land in eastern Loess Plateau. *Catena, 199*. https://doi.org/10.1016/j.catena.2020.105107

Yao, H., He, Z., Wilson, M. J., & Campbell, C. D. (2000, 2000/08/01). Microbial Biomass and Community Structure in a Sequence of Soils with Increasing Fertility and Changing Land Use. *Microbial Ecology, 40*(3), 223-237. https://doi.org/10.1007/s002480000053

Zachara, J., Brantley, S., Chorover, J., Ewing, R., Kerisit, S., Liu, C., Perfect, E., Rother, G., & Stack, A. G. (2016). Internal domains of natural porous media revealed: critical locations for transport, storage, and chemical reaction. *Environmental Science & Technology, 50*(6), 2811-2829.

Zhang, Y., Yang, Z., Wang, F., & Zhang, X. (2021). Comparison of soil tortuosity calculated by different methods. *Geoderma, 402*, 115358.

Zheng, Q., Hu, Y., Zhang, S., Noll, L., Bockle, T., Richter, A., & Wanek, W. (2019, Jan). Growth explains microbial carbon use efficiency across soils differing in land use and geology. *Soil Biol Biochem, 128*, 45-55. https://doi.org/10.1016/j.soilbio.2018.10.006