Impacts of pH on mechanisms and rates of carbon and nitrogen mineralisation: a review

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This research was funded by the Foundation for Applied Water Research (STOWA) and the Dutch Ministry of Agriculture, Nature and Food Quality (project number KB-24-002-024).

Wageningen Environmental Research
Wageningen, March 2024

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Report 3342
ISSN 1566-7197

WAGENINGEN
UNIVERSITY & RESEARCH

Breugem, A.J., J. Kros, W. de Vries, 2024. *Impacts of pH on mechanisms and rates of carbon and nitrogen mineralisation: a review on.* Wageningen, Wageningen Environmental Research, Report 3342. 60 pp.; 28 fig.; 2 tab.; 151 ref.

Decomposition of soil organic matter (SOM) plays an important role in nutrient (re)cycling in all ecosystems of the world. Decomposition of SOM in soils is mainly a soil microbial process. Soil pH affect many soil characteristics which in turn affect the microbial indicators, such as microbial composition, biomass and growth and thereby the microbial activity. This activity governs the mineralisation processes of soil organic matter and is strongly pH dependent. This report gives first an overview of the mechanisms behind impacts of pH on these microbial indicators as well of the impacts of pH on microbial indicators themselves of which pH influences on the major decomposition process do get much attention. Next, it presents empirical quantitative relationships between pH and the mineralisation processes respiration, ammonification and nitrification. Finally, the report gives recommendations on how to include pH dependent relationships in SOM decomposition models.

Keywords: decomposition, mineralisation, nutrient cycling, nutrient availability, contaminant toxicity, soil structure, soil organic matter, pH, microorganisms, microbial biomass, microbial growth, microbial activity, respiration, ammonification, nitrification

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Wageningen Environmental Research Report 3342 | ISSN 1566-7197

Photo cover: Shutterstock

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Verification

Report: 3342
Project number: KB-24-002-024

Wageningen Environmental Research (WENR) values the quality of our end products greatly. A review of the reports on scientific quality by a reviewer is a standard part of our quality policy.

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date: 15 March 2024

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name: Gert Jan Reinds

date: 15 March 2024

Preface

Though the influence of pH on decomposition and mineralisation has been investigated frequently, this influence has not been investigated in-depth. With "in-depth" we mean that scientific results concerning this influence have not been compiled systematically to be able to obtain a universal description for the quantitative relationship between pH and soil organic matter decomposition. The study presented aims to give a stimulus to this systematic review of scientific results by initiation of thorough reflection among soil and microbiological scientists to come to a scientifically sound approach of the study on the pH dependable decomposition. At present, a universal description is highly recommended for the modelling of soil organic matter decomposition as the pH is one of the main soil indicators that influences this decomposition that is not incorporated in current decomposition models.

Summary

Decomposition and mineralisation of soil organic matter (SOM) play an important role in nutrient (re)cycling in all ecosystems of the world. Decomposition of SOM in soils is mainly a soil microbial process. pH is one of the main factors influencing this decomposition. In this study we want to investigate the quantitative relationship between pH and decomposition. Until now this relationship has not been studied systematically. In recent modelling studies there is an increasing one need to account for the pH influence on the decomposition and mineralisation of organic matter.

Regarding pH dependent decomposition we discern soil physical and chemical indicators as well as microbial indicators. Each set of indicators has its own indicators. For soil indicators these are: nutrient availability, contaminant toxicity, soil quality and soil structure. As microbial indicators we mention microbial composition, biomass/growth and activity. In this study the microbial activity has been expressed by mineralisation, ammonification and nitrification. The relationships between the different indicators and pH are given in a conceptual scheme.

Apart from direct pH effects on microbial indicators, most effects are indirect due to the influence of the pH on organic matter input and soil indicators. These indirect effects in turn affect the microbial community and thus microbial activity. As the microbial activity influences the pH of the soil, feedback loops between pH and the decomposition rate also exist.

The impacts of pH on the microbial community and the mechanisms behind this effect are reasoned in several ways. Changes in soil pH within a single soil type can have marked effects upon soil microbial biomass and microbial activity most likely due to increased extractable aluminium as soil pH decreases (indirect effect of pH on microorganisms). Another reason is the effect of pH on enzyme activities of the corresponding microorganisms (direct effect on microorganisms). Besides, pH dependencies of decomposition reaction rates can be affected by combined effects of aluminium toxicity, enzyme activity, and the decomposer community (both direct and indirect effects of pH on microorganisms).

For many processes, the overlapping abilities of microorganisms to decompose SOM provide a functional redundancy that allows terrestrial ecosystems to function over a broad pH range. This results into a modest, almost linear increase of SOM decomposition with pH. Ammonification and nitrification however, are carried out by only a few species of microorganisms. Therefore, the impact of pH on ammonification and nitrification is much greater than on respiration. Significant changes in nitrogen transformation rates are observed over relatively small pH increments. As a consequence, SOM decomposition can be characterised as less pH sensitive than ammonification and nitrification. This argues for the use of a distinct mathematic relationships for the pH dependent modelling of SOM decomposition (carbon dioxide production), ammonification (ammonium production) and nitrification (nitrate production).

From literature several quantitative pH-decomposition relationships are derived. Since the number of relationships derived is relatively low and the pH effect on decomposition is not yet systematically investigated a generalisation of the quantitative pH-decomposition relationship cannot be easily made. Given the conceptual scheme it is questionable if such a relationship can be derived for accurate modelling of carbon dioxide, ammonium or nitrate production: the pH influences soil processes in many ways with mutual dependencies, besides the process-specific pH response functions. This makes modelling of pH decomposition relationships not straightforward and also soil system dependent, though the soil dependency can be accounted for. Therefore, it is advised to determine a pH decomposition relationship for each soil system separately. However, the determination of such a relationship is not easy. Despite this generic relationship could be calculated which might provide rough production rates that could function as a first order quantification in a modelling study.

This study has also shown that other factors such as nitrogen deposition can overrule the pH effect, underpinning the importance of a system-based approach in decomposition modelling activities. In this case an independent use of process-specific pH response functions (as is the case in mutual dependencies) will not be sufficient. Another system-dependent factor is plant nutrient uptake or plant productivity. Since plant productivity interferes with nitrogen mineralisation, in view of pH, the net effect of an increased pH on ecosystem storage is difficult to predict without doing experiments. One of the factors -not incorporated in the conceptual scheme- that influences the behaviour of SOM is the influence of clay on the stabilisation of SOM. This stabilisation is pH dependent. The influence of the clay content can be substantial, we therefore recommend to take the clay content into account as a pH dependent factor in SOM decomposition models. We recommended not to solely focus on pH as a separate factor on the specific decomposition processes involved, but also to consider other decomposition relevant factors if they are pH dependent.

All in all, this study shows that modelling pH decomposition relationships is not easy and straightforward. We highly recommend that these relationships are further examined, both more systematically and fundamentally. In order to carry out such a comprehensive study, a broad scientific research programme has to be established. This research program needs to include the factors that interfere with the soil pH (like nitrogen deposition), the carbon and nitrogen balance of the soil (like nitrogen uptake by plants) and with the behaviour of SOM in various soil types under various climatic conditions.

1 Introduction

1.1 Background and aim

Decomposition, mineralisation and microbial indicators
Decomposition of soil organic matter (SOM) plays an important role in nutrient (re)cycling in all ecosystems of the world (Tiessen et al., 1994; Madejón et al., 2012; Soilhealth, 2012). It is fundamental for the on-going health and vitality of these systems. SOM decomposition is entirely dependent on the activity of soil microorganisms and is crucial for transfers and transformations of nutrients and as a result SOM soil content and nutrient availability to plants (Tian et al., 2008; Ictorganics, 2012). Besides its crucial role in nutrient recycling, SOM also plays an important role in the maintenance and improvement of soil properties like soil structure and soil cation exchange capacity (CEC). SOM stems from litter production from aboveground (leaves, twigs, fruits, branches, etc) and belowground (roots) plant material (Leifeld et al., 2013) and so depends on the primary production. Roots are the most important source for soil carbon (Rasse et al., 2005).

SOM decomposition is mainly a soil microbial process. The involved soil microorganisms can be divided in three major groups: fungi, actinomycetes and bacteria. Bacteria are the most abundant organisms playing an important role in the decomposition of organic matter. The majority of the bacteria involved in this decomposition are heterotrophs. The abundance of autotrophs is comparatively small and are not directly involved in SOM decomposition. Fungi also have an important role in organic matter decomposition (Wood, 1988; Tate, 2000; Horwath, 2007; Plante and Parton, 2007). The generation of microorganisms capable of decomposing organic material can be grouped according to the constituents of the vegetative material entering into the soil (Agriinfo, 2012). Therefore the latter are modestly discussed in this review. Generally speaking SOM decomposition by bacteria is dominated at a high pH whereas fungi dominate at a low pH. Several studies have found that a low pH is physiologically disadvantageous to bacterial growth, decreases bacterial abundance, and increases fungal growth (Rousk et al., 2009).

Box 1

Organic matter break down indicators
Decomposition is the conversion of SOM into its basic compounds by physical, chemical and (micro)biological processes.
Mineralisation is the conversion of SOM into its basic (or mineral) compounds by (micro)biological processes (thus mineralisation being a part of decomposition).
Respiration is the conversion of SOM into CO_2 by (micro)biological processes (thus respiration being a part of mineralisation).
Ammonification is the conversion of SOM into NH_4^+ by (micro)biological processes.
Nitrification is the conversion of NH_4^+ into NO_3^- by (micro)biological processes.

Microbial indicators
Microbial composition: the various groups of microbes (bacteria, fungi) and associated species occurring in a soil.
Microbial biomass: the mass of microbes in kg ha^{-1} or mg kg^{-1} occurring in a soil.
Microbial growth: the growth of microbes in kg ha^{-1} yr^{-1} or mg kg^{-1} h^{-1}.
Microbial activity:
- the activity of microbes in terms of the respiration rate in mg C kg^{-1}(soil) h^{-1} (basal respiration rate) or mg C g^{-1}C (microbes) h^{-1} (specific respiration rate);
- the activity of microbes in terms of the ammonification/nitrification rate in mg N kg^{-1}(soil) h^{-1} or mg N g^{-1}C (microbes) h^{-1} (specific ammonification/nitrification rate).

Above, several terms, used in microbial ecology, are introduced that need a proper definition. In order to get clear what we are talking about, we firstly give a description of various terms for organic matter breakdown, i.e. 'decomposition', 'mineralisation' and 'respiration' and microbial indicators in a glossary (see Box 1). Note that the definitions can differ somewhat from those given in the literature. For example, Wolf and

Wagner (2005) define decomposition as the chemical breakdown of a compound into simpler compounds, often accomplished by microbial metabolism and mineralisation the conversion of an organic form of an element into an inorganic form as a result of microbial decomposition. Generally considered, 'decomposition' is a somewhat wider term than 'mineralisation'. Besides mineralisation, decomposition includes pure chemical as well physical breakdown and breakdown by biota other than microorganisms.

Factors affecting decomposition

In short, the decomposition process can be schematized as in figure 1. The main decomposition products are CO_2, NH_4^+/NO_3^- and base cations (BC^{n+}) which in turn influence/determine the charge balance and so the pH of the soil solution.

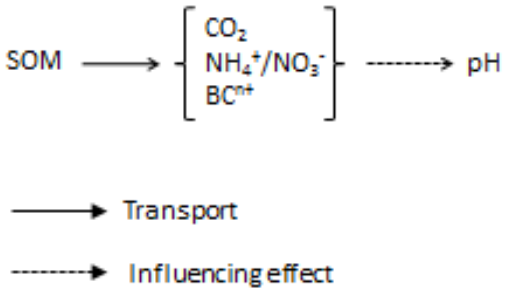

Figure 1 *Scheme of the decomposition process.*

Decomposition of SOM is basically determined by two factors: (i) quantity and quality of organic material entering the soil (chemical properties like C/N and composition (i.e. fractions differing in decomposability); physical properties like size and structure) and (ii) environmental conditions (clay content or CEC, temperature, soil moisture, aeration, texture, pH, fertility level such as C/N ratio and carbon and total nitrogen content of the soil, inhibitory substances, microbial biomass, and microbial community) in the soil (Jenkinson, 1981; Riffaldi et al., 1996; Kemmitt et al., 2006; Greencare, 2012; Zhu et al., 2013). Walse et al. (1998) ascribed litter decomposition to the combined effect of enzyme activities, decomposer community and Al^{3+} toxicity. The decomposition rate as well as potentially mineralisable carbon vary considerably among soils, reflecting differences in soil properties (Riffaldi et al., 1996).

Impacts of pH on decomposition

Soil pH is a basic soil property with a multitude of effects on soil and vegetation processes, influencing the availability of carbon, nutrients and toxic substances, the abundance and growth of plant species, the CEC and soil structure (Andersson et al., 2000; Kemmitt et al., 2005; Leifeld et al., 2013). Soil pH also determines the geographic pattern of soil bacteria (Fierer and Jackson, 2006), soil fungi (Tedersoo et al., 2014) and the microbial metabolic quotient (Xu et al., 2017). Furthermore, soil microbial activity and diversity or composition are impacted by chemical, physical and biological soil properties that are also influenced by pH, and are the dominant factors governing the microbial turnover of OM (Adams and Adams, 1983; Robson, 2012). Consequently, soil pH is one of the most fundamental variables in microbial ecology, influencing the structure, biomass, growth and activity of the soil microbial community (Crowley and Alvey, 2002; Rousk et al., 2010b; Madejón et al., 2012) and thereby their functioning in terms of carbon and nitrogen mineralisation. This holds for both forest and arable soils (Strickland and Rousk, 2010) as well as grassland soils (Rousk et al., 2011a). Most present models of carbon and nitrogen dynamics do not take the effect of pH into account, yet this is necessary to adequately simulate what is happening in natural and semi-natural environments (Motavalli et al., 1995; Leifeld et al., 2013), particularly those subjected to altered land management regimes or exposed to increased deposition of acidifying pollutants from the atmosphere (Foereid et al., 2006).

An inherent problem in studying soil pH effects on decomposition is the multitude of direct and indirect effects on soil microorganisms (Tate, 2000). The direct effects relate to metabolic and enzymatic microbial activities and the indirect ones to the soil microbial biomass (Li et al., 2019). The direct and indirect effects are hard to separate due to their complex interactions (Tian et al., 2008; Rousk et al., 2009). In addition, when pH effects of different natural soils are compared, confounding factors derived from differences in soil type and management will be introduced. Malik et al. (2018) showed in an empirical study in the UK, that a pH threshold exists at which effects of land management on microbial cycling (microbial carbon use efficiency and carbon turnover rate) changes. In near-neutral pH (around 6.2) a greater proportion of organic substrate is allocated to microbial biosynthesis and growth, and therefore greater carbon storage. This allocation is aided by less intensive land management practices. In acidic wet environments, however, biosynthesis and growth as well as substrate decomposition are limited as a consequence of stress and substrate limitation. Hence, SOC accumulates as substrate. When however, land management intensifies, acid and wetness related retardation of microbial biosynthesis/growth and of morganic matter decomposition diminishes, by which large losses of carbon through microbial decomposition arise.

Considering the large number of direct and indirect effects of pH on decomposition and the variability of pH in space and time, the modelling of SOM decomposition is not straightforward. Accurate mechanistic modelling of soil carbon and nitrogen mineralisation and their responses to the changes in the environments requires a detailed understanding of the factors that control or influence these biogeochemical processes (Ouyang et al., 2008). Most models, however, use an empirical lumped description of pH effects on decomposition, if considered at all, such as the case in wide spread carbon dynamic models CENTURY (Parton, 1996) and RothC (Coleman and Jenkinson, 1996). There is a need to improve the pH – SOM decomposition relationship in models as there is a growing evidence that the pH influence is a major factor controlling decomposition of SOM (e.g. Leifeld et al., 2008; Cheng et al., 2013; Tian et al., 2013) and the current relationships used in models so far, such as e.g. SMART2 (Kros et al., 2016) and VSD+ (Bonten et al., 2011) are not satisfactory as they lack complete scientific support. Moreover, more insight in the mechanisms behind the pH effects is needed as a basis to (assess whether it is possible to) further improve modelling of pH impacts on SOM decomposition. The evidence of a strong pH effect (or the regulatory role) on decomposition rates is given by Leifeld et al. (2008) and Walse et al. (1998): decomposition rates can vary by a factor of four in the pH range from 4.0 to 6.0 as shown in figure 2.

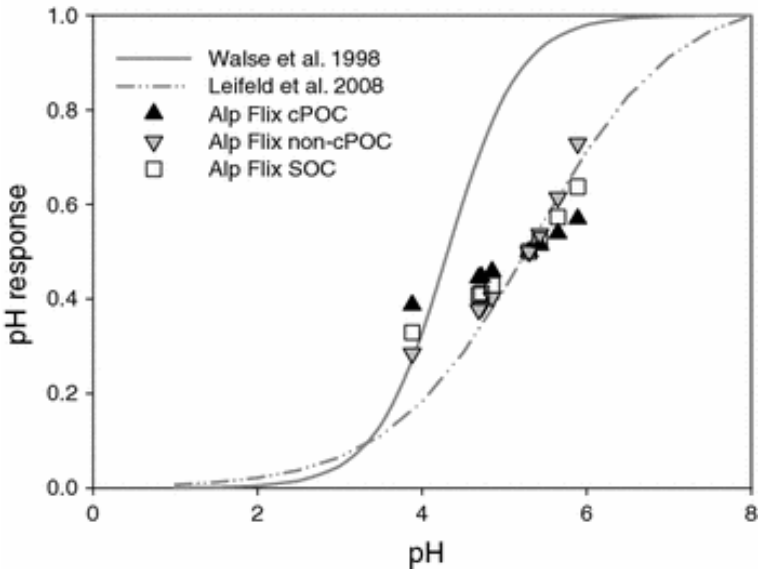

Figure 2 *Comparison of pH response as function of pH for litter decomposition (Walse et al., 1998), cPOC turnover (Leifeld et al., 2008)), and for bulk soil carbon, cPOC and non-cPOC from the study of Leifeld et al. (2013). The midpoint of the sigmoid (i.e. pH response equals 0.5) was assumed to be the same as in the function of Leifeld et al. (2008). From: Leifeld et al. (2013).*

Aim of the study
In this study we investigated the influence of pH on SOM decomposition, focusing on both carbon - and nitrogen mineralisation. The aim of this review is twofold.

The first aim is to understand this relationship (all relevant factors and processes) through a thorough analysis of the available literature about the decomposition of organic matter and its pH dependency, a process-based approach. The question is: which fundamental processes determine the pH effect of/on decomposition of soil organic matter?

The second aim is to empirically quantify the overall pH effect function for decomposition and mineralisation in view of modelling purposes based on experimental data from literature by which quantitative relationships between pH and decomposition can be determined. The questions formulated above will be examined separately for carbon and nitrogen mineralisation since these are generally modelled separately including SMART2 (Kros et al., 2016) and VSD+ (Bonten et al., 2011).

1.2 Overall concept

The influence of pH on carbon and nitrogen mineralisation via soil microorganisms (biological decomposition) is determined via several indicators, related to soil as well as microorganism (figure 3). Regarding soil indicators we make a distinction between nutrient availability, contaminant toxicity and soil structure. Microorganism indicators are divided in community composition and Biomass/growth. These indicators are dealt with in paragraph 2.2 and 2.3 respectively.

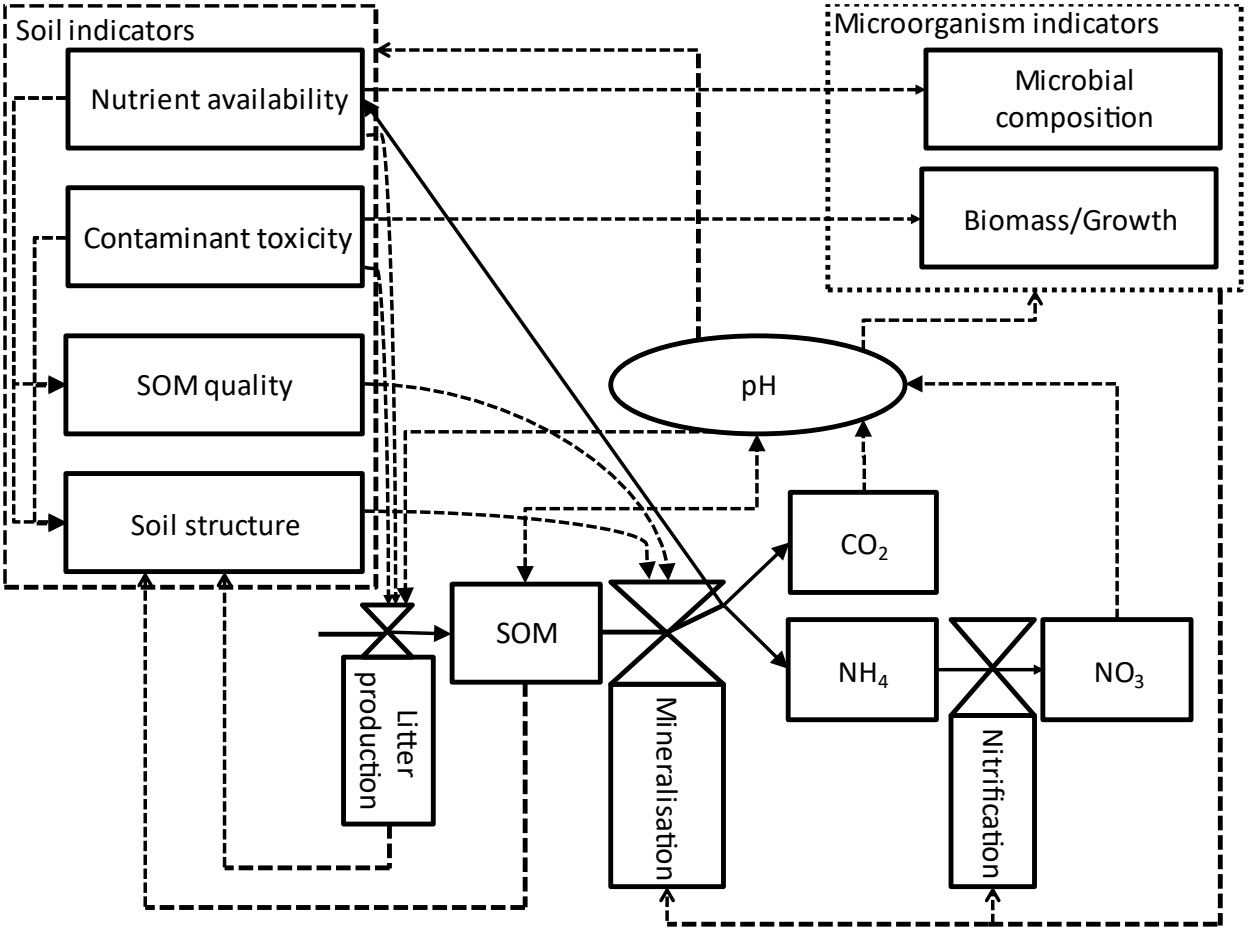

Figure 3 *Soil pH affects soil and microorganism indicators which in turn affect litter production (both aboveground and belowground) or/and mineralisation and nitrification that on their turn affect soil pH. This figure includes all direct as well as most indirect effects of pH on SOM decomposition.*

Nutrient availability and contaminant toxicity determine the rate of litter production, SOM quality, soil structure, and composition and biomass/growth of the microorganisms. The composition and biomass/growth of the microorganisms in their turn determine the rate of mineralisation and nitrification. Litter production, mineralisation and nitrification subsequently influence the pH of the soil. In turn the pH influences the indicators of the soil and those of the microorganisms. pH influences the input of SOM by affecting both plant- and microbial growth and therefore litter production (both aboveground and belowground). SOM itself influences pH and soil structure. These relations and feedback loops, being relevant for our study, are graphically depicted in figure 3. This figure shows the crucial (indirect) role of pH on the production of the inorganic substances CO_2, NH_4 and NO_3 from the decomposition of organic matter (Raubuch and Beese, 1995; Bardgett and McAlister, 1999; Anderson, 2003; Soilquality, 2012).

It is important to consider that microorganisms themselves contribute to soil acidity (by mineralisation and nitrification), or have the ability to alter soil pH (Hartel, 2005). The same is applicable to SOM. SOM production itself, nitrification of ammonium, and CO_2 dissolution into water all add to acidification of the soil (Crowley and Alvey, 2002; Soilquality, 2012). If soils become more acidic, microbial activity slows down and so does SOM decomposition. In soils with a large SOM content, the pH will be buffered (pH increases or decreases less rapidly); in fact SOM itself plays a role in regulating the acidity (FAO, 2012). Apparently, both the functioning of soil microorganisms and SOM are part of a feedback loop, complicating the picture of pH effects on microbial functioning i.e. the processes mineralisation, ammonification and nitrification.

Another positive feedback loop concerns the effect of the microbial community structure in the soil. A well-functioning soil microbial community requires an adequate soil pH causing a faster rate of OM turnover. Furthermore, it promotes a good soil structure which in turn enhances biological activity and a further improvement of the soil structure (Tardy et al., 2014; Cui and Holden, 2015).

Finally, an increase in pH generally increases plant productivity (Hobbie and Gough, 2004; Foereid et al., 2006), thus causing a higher organic matter input by increased litter production / fall as well as increased root runover.

Soil pH influences the activity of the microbes both *directly* and *indirectly* and therefore the rate of carbon and nitrogen cycling. *Directly* i.e. by influencing the microbes themselves (the microbial indicators; e.g. inhibiting certain members and thereby the microbial composition) and *indirectly* i.e. by influencing factors that in their turn have an influence on microbial functioning (mechanisms behind the microbial indicators; e.g. the increase of Al in the soil solution that reduces substrate bioavailability and induces toxicity). Apart from (direct) pH effects on microbial indicators i.e. microbial composition, biomass/growth and activity, most effects are indirect due to the effects of pH on organic carbon inputs (litter production or quantity) and on soil indicators specifically nutrient availability, contaminant toxicity, soil structure and SOM quality (see also figure 3).

The mechanisms behind these impacts will be discussed in section 2.2, while the impacts of pH on the microbial indicators themselves will be dealt with in section 2.3. Sections 2.4 and 2.5 specifically deal with the influences of pH on the microbial activity indicators: respectively carbon mineralisation and nitrogen mineralisation. The concept of functional redundancy does get specific attention in 2.4 as it appears to be fundamental in explaining the relation between pH and respiration. Section 2.5 has been split up in studying the pH influences on the separate processes ammonification and nitrification, explaining the conditions when ammonium, nitrite or nitrate accumulates.

1.3 Study approach and outline of the report

Study approach

In order to understand the influence of pH on SOM decomposition, several indicators were used. The indicators used are based on basic microbial indicators, i.e. microbial composition, microbial biomass/growth and microbial activity. For the study of the quantitative relationships between pH and decomposition we choose three specifications of the basic microbial indicator microbial activity: respiration rate, ammonification rate and nitrification rate. The indicators mentioned are subscribed in the glossary above.

As a first step we made a general inventory on mechanisms behind the influence of pH on SOM decomposition by (i) searching on the Internet both search engine Google and the program Web of Science and (i) by consulting chapters in major handbooks like those of Hartel (2005) and Horwath (2007). This delivered a rough framework about the influence of the pH on OM decomposition in soil.

Next, scientific literature was collected via 'Web of Science' using the keywords 'pH', 'decomposition or mineralisation', and 'soil organic matter' in December 2013 and October 2023. This resulted in 1309 articles. All articles were screened using the title (using the abstract for further clarification) in order to make a first selection of relevant papers. This resulted in 111 articles of potential / possible interest. These articles included in the review if they complied with the following three inclusion criteria;

- The article must have information about a clear connection with pH or a pH gradient – in both natural and experimental environments (laboratory or greenhouse) either nor with quantitative data (see e.g. Kemmitt et al., 2006);
- The article examines specifically decomposition of organic matter, carbon- or nitrogen dynamics and, mineralisation as expressions of microbial activity;
- Organic matter used in the experimental work must originate from plant material in agricultural or natural ecosystems. Articles on the decomposition of separate plant constituents, like lignin - and anthropogenic organic substrates, like sewage sludge were not considered.

After thorough examination of the 111 articles above using these inclusion criteria we ended up with 27 articles that we included in the review. Additional articles, based on prior experience in the field as well as relevant book chapters were also included. This resulted in a total of 76 articles on which this review is based.

Outline of the report

This report is structured as follows: in chapter 2 insight on the mechanisms involved in the impacts of pH on microbial indicators, and thereby on C and N mineralisation are presented. This is summarised in a conceptual scheme, showing (in)direct effects as well as feedback loops. Additionally a general overview is given on the effect of pH on the different groups of microorganism (i.e. bacteria, fungi, archeae) in soils, their composition, mass and activity. Attention is also paid to feedbacks loops present in the soil system. Chapter 3 deals with the empirical quantitative relationships found between the pH and C and N mineralisation. Some attention is also given to the environmental factors that influence the C and N mineralisation processes like soil type and soil temperature because these factors co-influence these processes. In chapter 4 recommendations and considerations are given to deal with the pH in models of SOM decomposition and some ideas are presented for further research.

2 Impacts of pH on microbial indicators and their underlying mechanisms

2.1 Mechanisms behind the effect of pH on microbial indicators

2.1.1 pH and organic matter input (litter quantity)

Aciego Pietri and Brookes (2009) demonstrated a litter quantity effect in an experiment at which they added straw or no straw along a pH gradient in Rothamsted Research, UK (Hoosfield acid strip). Besides a straw effect they also discerned a pH effect as well as an interaction effect on the CO_2 production: this production increases with a higher pH and with addition of straw; the pH effect was different for the addition of straw and without it. At pH > 4.5, this addition stimulated bacterial biomass more than it did the fungal biomass, while at pH < 4.5 it does not change fungal biomass proportions. Though straw addition increased microbial biomass, this increase was less pronounced in low pH soils indicating a direct pH effect as well as a substrate effect. Although exchangeable Al increased considerably at low pH, unexpectedly the largest relative increases in microbial biomass and CO_2 production occurred just at these low pH's. As a possible explanation, Aciego Pietri and Brookes (2009) suggest that the effects of pH on biomass differ from the direct or indirect effects by Al due to pH. Addition of straw in an acid red soil increases the soil organic carbon mineralisation because of an increase in the bacterial and fungal abundance and diversity. This increase of soil organic carbon mineralisation takes place despite the decrease in pH by the addition of straw (Xiao et al., 2018).

2.1.2 pH and nutrient availability

The availability of most microorganism-essential nutrients is pH dependent. Microbial functioning depends on the nutrient availability, this availability regulates the microbial activity of the microbial groups/species concerned. Lack of nitrogen particularly slows down the decomposition of organic matter (Agriinfo, 2012). This lack arises when the C:N:P stoichiometry of the microbial biomass significantly differ from the C:N:P stoichiometry of the soil (Griffiths et al., 2012). The majority of microorganisms thrive in neutral pH due to the high availability of most nutrients in this pH range, but there are examples of microorganisms (esp. fungi) that can tolerate pH 1 - 13 (Microbewiki, 2014). Nutrient availability does not only influence the microorganisms themselves i.e. the microbial behaviour or activity, it also influences the behaviour of the organic matter which influences microbial activity too. In this respect the concentration hydrogen ions and polyvalent cations are important in determining the solubility/stability of organic matter and thus the possibility for microbial attack (Hernandez-Soriano et al., 2013). While at low pH hydrogen bonding among organic matter molecules reduces their solubility, higher pHs (>5) deprotonate these molecules increasing their solubility as a result of a decrease of the bonding between organic compounds and soil particles (destabilisation) (Sollins et al., 1996). In this way these molecules become more available for the microorganisms in the form of dissolved molecules where they becomes less resistant to degradation and more accessible to microorganisms and soil enzymes (Sollins et al., 1993). It can also increase the availability of binding sites for polyvalent cations stabilising them (Whittinghill and Hobbie, 2012). Therefore the net effect of changes in pH and polyvalent cations on the fate of organic matter is not straightforward. Liming, for example, *can* enhance soil respiration as well as nitrogen mineralisation (Curtin et al., 1998).

2.1.3 pH and contaminant toxicity

The availability (dissolved concentrations) and thereby the toxicity of contaminants are affected indirectly by soil acidity. Under acidic conditions, organic acids are toxic to microbial growth due to their chemically neutral state. Another indirect effect of soil pH concerns the solubilisation of toxic compounds or elements (Tate, 2000). Alkaline soils do not give problems to microorganisms in view of toxic levels of elements. On the other hand, acidic soils become rich in Al, Mn and B and reach toxic levels to microorganisms (Agriinfo, 2012). The free heavy metals and metalloids present in the ionic form at elevated concentrations in the soil

solution may be toxic to these microorganisms. These metals may inactivate extracellular enzymes responsible for organic matter decomposition. As nitrification results in acidification of the soil (Amoo and Babalola, 2017), it contributes to aluminium toxicity. Due to additional production of protons, nitrification in acidic soils can even lead to further acidification and aluminium toxicity (Li et al., 2018).

It is very likely that the decrease in microbial biomass at lower pH values is caused by Al-toxicity (Aciego Pietri and Brookes, 2008b). Al-toxicity can be observed as a reduction in the proportion of microbial biomass carbon to total organic carbon (2 to 4% in neutral soils, 1% in strongly acidic soils) suggesting that organic matter decomposition is impaired at very low pH as this decomposition is related to the microbial biomass. Mechanisms involved are a decrease of carbon inputs from plants to soils and a decrease in conversion efficiency of this carbon into biomass carbon. Soils with a high pH especially with an increased clay and organic matter content have considerably reduced metal toxicities facilitating especially the group of the bacteria (Crowley and Alvey, 2002).

2.1.4 pH and soil structure

pH has an influence on soil structure as it influences 1) the deprotonation of organic matter and 2) the availability of polyvalent cations (2.2.2). As a high pH promotes the deprotonation and increases the availability of polyvalent cations, the quantity of front-plate coupling of clay plates will increase and so soil structure will improve at high pH. In this way a higher pH will facilitate the soil oxygenation and so the O_2 availability to microorganisms and so the decomposition (Hartel, 2005; Voroney, 2007). Otherwise, the microbial activity related to decomposition affects the soil pH and so the soil structure. Hence, one can imagine that a structure-related pH optimum exists in view of the microbial biomass/presence of microbial species.

The rate of decomposition is higher in neutral soils than that in acidic soils (Agriinfo, 2012). A decrease in pH causes a decline in of the CEC of clay and so the destabilisation or protection of organic matter by binding to clay (Trumbore, 1997; Tate, 2000; Plante and Parton, 2007) slowing down the mineralisation.

2.1.5 pH and quality of soil organic matter

Besides the influence of pH on the amount of SOM input, there is also the influence of the quality of this OM and of the selective preservation or metabolic modification of specific components during decomposition (van Bergen et al., 1998). Besides pH, plant species also have an effect on the decomposition. Hobbie and Gough (2004) e.g. observed that variations in plant species composition have the potential to affect soil carbon and nutrient cycling because of species differences in litter chemistry (i.e. quality) and thus decomposition and nutrient dynamics. Both the quantity and the quality of SOM influence on their turn the composition and functioning of the microbial community (Madejón et al., 2012).

Soil pH not only affects the quality of the organic matter input (i.e. plant or litter quality) into the soil, it also affects the physical and chemical quality of organic matter in the soil (Kemmitt et al., 2006). A well-known quality parameter of SOM that affects carbon and nitrogen during decomposition, is its C/N (Li et al., 2007; Manzoni et al., 2008) with an optimal C/N for decomposition of 24 in view of nitrogen immobilisation (Chen et al., 2003). According to Booth et al. (2005) differences in production and fate of mineralised nitrogen among ecosystem types result primarily form differences in composition and concentration of soil organic matter.

Another relevant parameter is the solubility of organic matter: response of mineralisation rates to pH changes might also be related to changes in the size of the pool of mineralisable organic matter. Generally, soil organic matter solubility increases with increasing pH due to the increasing number of negative charges on both organic matter and other soil components (Whittinghill and Hobbie, 2012). The concentration of polyvalent cations and soil pH interact to affect solubilisation of soil organic matter and therefore microbial activity. These cations bind organic molecules together and to minerals. In soils with low Ca and high Al levels (acid conditions) strong bonds are formed between Al and SOM functional groups that will increase protection and so decrease soil organic matter decomposition; in soils where pH is mainly controlled by Ca (neutral or alkaline conditions), the opposite applies (Clarholm and Skyllberg, 2013). It is widely known that

liming increases dissolved organic matter (Curtin et al., 1998; Garbuio et al., 2011). Curtin et al. (1998) explicitly mention the increased availability of organic substrates to soil micro-organisms, next resulting into increased nitrogen fertility. The concentration of polyvalent cations and soil pH interact also to affect stabilisation of soil organic matter and therefore microbial activity. As the bond between these cations and organic matter is not easily reversible, they prevent the microbiological breakdown of organic matter.

2.1.6 Direct pH effects

The pH itself, specifically the proton concentration, directly influences microbial indicators. From Rousk et al. (2010a) it appears that the microbial composition is specifically related to pH (and not to nutrient availability, plant community or other auto-correlated factors). To exclude adaptation to the field pH, Fernández-Calviño et al. (2011) showed that the microbial composition grows best at the pH it is found at, providing evidence for a direct pH influence on this composition. In follow-up experiments to their initial pH-gradient work, Rousk et al. (2010b) showed that added additional plant material and nutrients did not stimulate the microorganisms at all pH values, suggesting that competitive interaction between fungi and bacteria could be responsible for indirect pH effects. Fungi do not seem to show a direct pH dependence, but rather an indirect one mediated by competitive interaction by bacteria being superior competitors. This can be explained by the different cellular physiology: fungi have mitochondria where proton gradients generate power, while bacteria need to maintain proton gradients with their environment to achieve similar power.

Protons directly affect the biomass/growth of the bacteria and indirectly of the fungi (Rousk, pers. comm.) The same holds for the respiration as microbial activity. According to Rousk et al. (2011b), respiration is more constrained by carbon supply or availability than by the microbial biomass/growth. Therefore, respiration is less acutely affected by pH than ammonification and nitrification are.

2.1.7 Interaction of different indirect pH effects: confounding factors

When studying the relationship between pH and mineralisation one quickly meets the problem of confounding factors. pH can have seemingly different effects on / relationships with mineralisation as it is confounded with other factors in the field. After Crowley and Alvey (2002): in the field one sees the overall effect of all factors working together.

Hobbie and Gough (2004) experienced the confounding effect of nutrient availability in the pH – mineralisation relation. They observed differences in litter decomposition between acidic and non-acidic Alaskan tundra sites: acidic sites counterintuitively have higher mineralisation rates than non-acidic sites. They also observed greater nitrogen availability and greater plant biomass at acidic sites than those at non-acidic sites with higher concentrations of basic cations. The large differences in plant species composition unexpectedly had negligible effect on litter decomposition compared to site differences in other factors influencing the environment. They presume that site differences in pH and nitrogen availability play a role. Higher soil nitrogen availability at the acidic site may have contributed to faster mineralisation, as this influence of nitrogen on mineralisation could have been observed in a fertilisation experiment. In addition, lower pH in acidic sites may influence the microbial community structure by promoting the part of fungi, probably increasing the decomposition rate at that site. This study confirms the importance of controlled experiments (i.e. lab experiments) if you want to confirm pH effects on mineralisation while excluding other factors as well as interactions between pH and other factors. Ouyang et al. (2008) found similar interactive effects; they observed enhanced emission of CO_2 at soils treated with simulated acid rain. Noticeably, the mineralisation of soil organic carbon and nitrogen was related to the contents of soil organic carbon and nitrogen, and not to initial soil pH and changes in pH due to simulated acid rain. The results indicated that acid rain could influence the mineralisation of organic carbon in acid soils by changing soil organic carbon and nitrogen status, rather than soil pH alone. Besides the low pH of the soils, Ouyang et al. (2008) explain the results by adaptation of the microbial community to the chronic acid rain conditions and by effects on the nutrient supply.

2.2 Impacts of pH on microbial indicators

As discussed in 2.2, different mechanisms of pH are present that indirectly affect different microbial indicators of the microorganisms involved in the mineralisation process and thereby the rate of mineralisation. The indicators used to gain insight in the cause of those processes/relationships are microbial composition, microbial biomass, microbial growth and microbial activity and are subscribed in the glossary above. In 2.3 we summarize the overall impacts of pH on the indicators microbial composition, microbial biomass, and microbial growth, indicating which mechanisms are relevant for those relationships. Next, in 2.4 and 2.5 we summarize the overall impacts of pH on the microbial activity indicators as specified by respiration rate, ammonification rate and nitrification rate. Finally, in 3.1 and 3.2 these rates are used for studying respectively the quantitative relationships between pH and carbon mineralisation and nitrogen mineralisation.

2.2.1 pH and microbial composition

pH and microorganism groups
Soil microorganisms are influenced by soil pH (see e.g. Kooijman et al., 2009). This is especially the case for bacteria, the most abundant group of soil microorganisms. Most of the soil bacteria prefer a neutral or slightly alkaline soil (pH between 6.5 and 8). Under acid conditions, bacterial biomass and/or growth as well bacterial activity is greatly reduced. Soil pH also influences the species of bacteria present in soil. Nitrifying bacteria for example, are absent or inactive in acid soils. Actinomycetes, the second most abundant group of soil microorganisms, prefer neutral/slightly alkaline soil conditions and do not tolerate acid conditions (pH < 5) well (Wolf and Wagner, 2005). Soil fungi (the third most important group of microorganisms)are generally less affected (in biomass and activity) by low pH than bacteria and grow in acidic soils (pH between 4.5 and 6.5). According to Wolf and Wagner (2005) most fungi are acid tolerant and are commonly found in acid soils. Fungi become more important than bacteria at low pH (Cheng et al., 2013). This fungal dominance promotes SOC storage (i.e. storage in fungal biomass) due to its higher carbon use efficiency compared to bacteria (Strickland and Rousk, 2010). This microbial efficiency plays a crucial role in carbon stabilisation (Cotrufo et al., 2013). In most cases however, bacteria are responsible for most of the decomposition of SOM. As a rule this process is markedly slower if pH drops below 6.0 (Soilquality, 2012). Most of the microorganisms grow best at pH 6 – 8, but are severely inhibited at pH < 4.5 and pH > 8.5 (Agriinfo, 2012). Furthermore, there are even differences within one species in tolerance of acidity (Soilhealth, 2012). An overview of the optimum pH range for the most important microorganism groups is given in table 1 (taken from Soilquality, 2012).

Table 1 *Maximum, minimum and optimum pH values for major microorganism groups.*

Microorganism group	Range	Optimum
Bacteria	5 - 9	7
Actinomycetes	6.5 - 9.9	8
Fungi	2 - 7	5

Bacteria involved in SOM decomposition are (mainly) aerobic and heterotrophic in nature. They degrade all sorts of organic substances present in organic matter (Plante and Parton, 2007; Robertson and Groffman, 2007). The same holds for the actinomycetes, though degrading the more resistant and indecomposable organic matter. Lignin and cellulose, resistant to decomposition by bacteria, are mainly decomposed by fungi, being the basis of their organic recycling role (Agriinfo, 2012). Besides relatively resistant material, they can decompose dry material as well (Mainlandminerals, 2012). They are particularly important in woody ecosystems and they are dominant carbon and nutrient recyclers of forest debris (Ictorganics, 2012).

Microorganism groups determining composition
In literature, the microbial composition mainly deals with the bacterial and the fungal composition. Regarding bacteria, information on the effects of pH on the soil bacterial composition at different values of pH is limited. However, shifts in composition are grossly related to pH, indicated by the fact that the bacterial communities

that develop in acid soils are well adapted to the prevailing pH, suggesting a shift to specifically adapted species (Crowley and Alvey, 2002). The growth of bacterial communities are positively correlated to soil pH, demonstrating its direct influence on the soil bacterial community. The soil pH appears to exert a strong selective pressure on the bacterial community growth, optimising it for the actual pH level in the soil (Fernández-Calviño et al., 2011). The dominance of pH in structuring bacterial communities appears from the strong connection between pH and the bacterial community composition, both across a single soil type in which the other soil indicators vary minimally and across biomes in which many soil and site indicators other than pH also change. The strong relationship for bacteria is explained by the narrow pH optima for bacteria strains (Rousk et al., 2010a).

The fungal community composition is also related to pH, but the influence is far weaker than for the bacterial community. This can be explained by the wide pH optimum of the fungal species and the competitive influence form the highly dynamic bacterial community along the pH gradient. Fungi can sustain low pH better than bacteria, use available carbon sources more efficiently and play a dominant role in the early decomposition process (Blagodatskaya and Anderson, 1998). Only when an appropriate measure of the microorganisms' functional impact is used, pH may indeed be strongly dictating the microbial community composition; growth does differentiate in view of pH but biomass does not between microbial decomposer groups (Strickland and Rousk, 2010).

According to Leifeld et al. (2008) it is likely that the microbial communities differ between sites as a direct response to pH because pH optima for microbial growth differ among microbial species. Any difference in the microbial community will thus shift the (pH response of) organic matter decomposition.

2.2.2 pH and microbial biomass

As soil microorganisms differ in their acidity tolerance, the relative bacterial, fungal and actinomycetal biomass is strongly affected by pH (Dpi, 2012). The diversity of heterotrophic bacteria in soils is great. This provides a buffer to pH effects on the total soil microbial biomass, even though individual species may be quite severely affected (Crowley and Alvey, 2002).

Soil-pH appears to exert a dominating influence on the incorporation of organic matter into microbial biomass (Wardle, 1992). Microbial biomass generally increases with pH over the pH range 3 – 7 due a decrease in aluminium and an increase in base cations concentrations presumably in the soil solution (Raubuch and Beese, 1995; Crowley and Alvey, 2002). Aciego Pietri and Brookes (2008a) observed a positive relationship between soil pH and microbial biomass over a very wide soil pH range (3.7 – 8.3) within a single soil type. In turn mineralisation of ammonia and conversion of ammonia to nitrate are strongly correlated with the size of the microbial biomass (Crowley and Alvey, 2002; Booth et al., 2005; Myrold, 2005). Neale et al. (1997) remarked that increased biomass may favour nitrogen immobilisation. Thus microbial biomass is important in soil nitrogen cycling as both a transformation agent and a source/sink of nitrogen.

In their study about carbon and nitrogen dynamics in agricultural soils, Kemmitt et al. (2006) found that soil microbial biomass carbon and nitrogen were positively correlated with soil pH in a pattern similar to the observed soil respiration, indicating a link between microbial biomass and microbial activity. Li et al. (2007) found this too in naturally (salt-affected) sandy soils and Tian et al. (2008) in the karst region of China, while Pankhurst et al. (2001) did not find an effect in Australian soils. Apparently, this relationship is not always straightforward.

The trend in soil microbial biomass carbon and pH is similar to that of soil microbial biomass nitrogen; therefore the C/N of the microbial community is not significantly affected by pH (Kemmitt et al., 2006) or it decreases with increasing pH (Li et al., 2007). This decrease indicated that increasing alkalinity of (saline) soils possibly favoured the bacterially-dominated microbial community and hence it favoured an increase in the total size of microbial communities. This is the case because the C/N is around five, six and ten for bacteria, actinomycetes and fungi respectively (Chen et al., 2003).

2.2.3 pH and microbial growth

Rousk et al. (2009) investigated this interaction by assessing how the relative importance of fungi and bacteria was affected by soil pH, at the well-known Hoosfield acid strip on arable fields at Rothamsted Research, UK). To avoid confounding factors This strip has a pH gradient from pH 4.0 - 8.3, with a uniform history of management regimen and the same soil type.

Rousk et al. (2009) showed that neutral or slightly alkaline conditions favoured bacterial growth while acidic conditions favoured fungal growth. From pH 8.3 - pH 4.5 there were opposing pH effects on fungal and bacterial growth: growth-based measurements revealed a fivefold decrease in bacterial growth (figure 4a) and a fivefold increase in fungal growth (figure 4b), resulting in an approximately 30-fold increase in fungal importance as indicated by the fungal/bacterial growth ratio. Apparently the fungal: bacterial ratios exhibit a threshold relationship with pH.

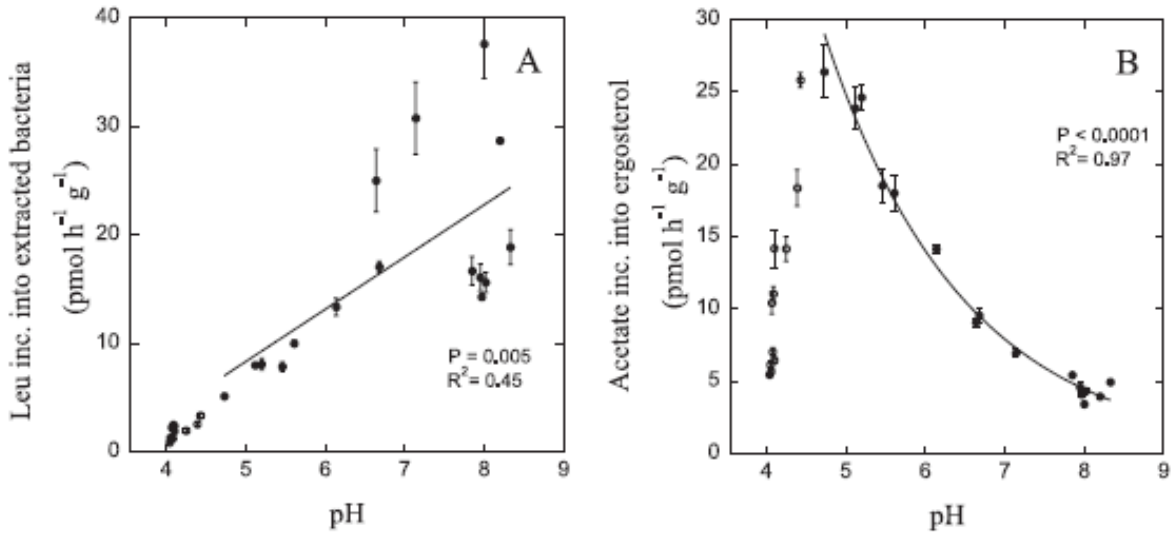

Figure 4 *(a) Effect of pH on bacterial growth (as measured by leucine incorporation; pmol h^{-1} g^{-1}) and (b) on fungal growth (as measured by acetate incorporation into ergosterol; pmol h^{-1} g^{-1}). The error bars indicate+/- standard error (n=3), inc.: incorporation. From: Rousk et al. (2009).*

Fungal growth, which increased with decreasing pH, decreased at pH < 4.5 (figure 4b). This inhibition is probably derived from increased inhibitory effects due to release of toxic free aluminium or from decreased plant productivity, that in turn decreases the availability of easily root-derived carbon as a substrate input (Aciego Pietri and Brookes, 2008a; Rousk et al., 2009). In contrast, the decrease in bacterial growth started at about pH 7, and continued gradually to pH 4 with no apparent additional effect between pH 5 and 4.

At a similar experiment in grassland soils ('Park Grass Experiment', Rothamsted Research, UK) Rousk et al. (2011a).Found that Bacterial growth decreased and fungal growth increased with lower pH, resulting in a factor 50 increase in the relative importance of fungi between pH 7.4 and 3.3. This factor is nearly two times larger than that at the arable fields.

Microbial growth and mineralisation are not directly linked since the partitioning of a substrate into growth and respiration varies, resulting in different growth efficiencies (Rousk et al., 2011a). Despite that, growth measurements provide more insight in decomposer group importance than biomass measurements (Rousk et al., 2009). This is in line with a two- to threefold difference in fungal biomass in the pH interval 8.3 - 4.5 compared to the 30-fold increase in fungal growth at the grassland soil experiment (Rousk et al., 2009) Similarly no difference in fungal biomass and a 50-fold increase in fungal growth over the pH interval 7.4 - 4.5 at the arable soil experiment (Rousk et al., 2011a).

3 Impacts of pH on carbon and nitrogen mineralisation

3.1 Impacts of pH on carbon mineralisation

This paragraph dealing with the effect of pH on carbon mineralisation is split up in two parts. The first part gives general remarks about the mineralisation process while the second part explicitly gives the quantitative relationships as discovered from field observations or lab experiments: how does the mineralisation rate change with pH?

3.1.1 Impacts on carbon mineralisation processes

In view of pH influences on the activity of microorganisms, the basic influence of pH concerns its influences on microbial enzyme activity (each enzyme has its pH-opt and pH-range), denaturation of proteins and the size and shape of organic particles (Tate, 2000). Generally, the enzyme activity directly regulating the net N mineralisation decreases with a higher pH (Li et al., 2019). The activity of carbon mineralisation enzymes differ slightly from that of nitrogen mineralisation (Aciego Pietri and Brookes, 2008b). Both exo- and endoenzymes play a role in this respect of which exoenzymes are probably the most rate limiting ones (Rousk, pers. comm.). According to Zhu et al. (2013) the production and consumption of inorganic nitrogen depend on activity and biomass of soil microorganisms and exoenzyme production. In addition, Leifeld et al. (2008) explicitly mention a major control of pH on exoenzyme activities during litter mineralisation. The carbon decomposition exoenzyme activity exhibits a threshold relationship with pH (Puissant et al., 2019).

Microbial activity can be altered - both naturally and artificially - by changing soil pH. An example of natural alteration concerns soil acidification by acid rain; see e.g. the study of Ouyang et al. (2008), discussed in 2.2.6. Liming of acid soils increases the activity of bacteria and actinomycetes and lowers the fungal activity (Agriinfo, 2012; Xiao et al., 2018): an example of artificial alteration of soil pH. In acid soils, liming decreases the fungal abundance/diversity as a direct consequence of pH increase and as indirect consequence of bacterial abundance/diversity increase. This change in microbial composition is accompanied by an increase in SOM mineralisation (Xiao et al., 2018).

The general range in soil reaction, pH 5 - pH 8, however, has only minor effects on the overall rate of decomposition. When one organism is repressed, another generally arises to take its place. This phenomenon is called *functional redundancy* (Crowley and Alvey, 2002; Rousk et al., 2009, 2011a). Crowley and Alvey (2002) described functional redundancy as: the effects of soil pH at the *process* level - causing shifts between bacterial- and fungal-dominated decomposition - manifest itself at the ecosystem level. If a microbial process like the mineralisation of organic matter is carried out by very wide range of species of soil organisms having overlapping roles there is a matter of functional redundancy. This provides for a continuity of mineralisation over a broad range of pH and results in a low pH dependency. Processes carried out by a few microbial species like those involved in nitrification, however, have greater dependency showing significant changes in transformation rate over relatively small pH increments (Crowley and Alvey, 2002; Soilhealthknowledge, 2012). Kemmitt et al. (2006) even speaks about the *level* of functional redundancy determining the impact of the community shift on SOM decomposition.

Li et al. (2007) make a distinction of the total SOM fraction (and associated C/N) into particulate and mineral-associated fraction (and their C/N 's) of native organic matter in soils. An increasing soil pH was associated with decreases in total soil organic carbon, nitrogen and the C/N, in particulate organic carbon, nitrogen and C/N, and in the C/N of the mineral-associated carbon. Apparently, soil pH is an important factor affecting soil organic carbon and nitrogen balances by means of the influence on microbial activity.

In soils of greater acidity (pH < 5) the presence of mineral-associated OM strongly reduces its turnover or its microbial availability. This pH-effect on the turnover of coarse particulate belowground OM is much weaker due to the relatively high root pH values. However, the availability of dissolved OM may be higher at low pH

in contrast to its real solubility due to a decline in the degree of metal-organic complexation with increasing acidity (Leifeld et al., 2013). Hence it is important to differentiate between labile coarse and older non-coarse particulate belowground OM fractions. In this respect roots are considered as important precursors for the labile coarse particulate belowground OM.

A study with ^{14}C and ^{15}N labelled substrates underpins the importance of pH on microbial activity: it shows that pH was the best soil-related predictor of decomposition parameters (Adams and Adams, 1983; Crowley and Alvey, 2002). Garbuio et al. (2011) summarised the effects of increased soil pH on carbon and nitrogen dynamics (in an Oxisol, obtained by liming) as increased microbial biomass, microbial activity, and bacterial/fungal ratio resulting in increased amino acid turnover, water soluble humic substances formation and increased nitrogen mineralisation and nitrification.

In a long-term experiment studying the effect of liming in an established pH gradient (3.77, 4.92, 6.39, 6.84), Abalos et al. (2020) discovered that liming increases the CO_2 emission (field respiration). They attributed this not only to increased abundance of microbes (Garbuio et al., 2011) and enhanced decomposition activity, but also to increased plant carbon inputs and root respiration. Notably, they did not observe differences in soil organic carbon contents between liming levels and attributed it to the compensation of increased CO_2 emission by higher plant carbon inputs. It appears that system-oriented approach is necessary to unravel the effects of pH on decomposition. This weighs even more as liming also affects the emission of other greenhouse gases: liming may decrease the N_2O emission due to increased N_2O reduction via nitrification and enhanced plant growth, and it also enhances CH_4 oxidation.

Elaboration on the effects of liming of acidic soils in more detail and more structured, shows that liming enhances/improves:

- Plant growth/productivity, favouring the production of roots exudates, the input of plant residues, and the autotrophic respiration as well as favouring the microbial abundance/activity;
- Soil structure, favouring the protection of SOC;
- Abundance of certain microbes like gram-negative bacteria (dependent on fresh, less-processed plant carbon, (Fanin et al., 2019), gram-positive bacteria (dependent on more-processed plant carbon (Fanin et al., 2019) and arbuscular mycorrhiza fungi (strongly influenced by plant carbon (Fanin et al., 2019), cellulose decomposing bacteria and microbes with a higher carbon use efficiency (and so a lower respiration);
- Microbial activity, favouring organic matter decomposition, increase of soil respiration (both autotrophic and heterotrophic respiration) (Ahmad et al., 2013).

All in all, SOC stocks as modified by liming (i.e. pH adaptation) eventually depend on the levels of its input (production by plant growth) and output (losses by respiration and decomposition). While short-term experiments show reductions of SOC stocks after liming, long-term experiments can show increases of SOC stocks because of the increased plant residue inputs progressively compensating the initial SOC losses attributed to increased mineralisation (Abalos et al., 2020). The decrease in total soil organic carbon with increasing pH can be largely attributed to the decrease in particulate organic carbon, as evidenced by negative relations between particulate organic carbon and pH and not between mineral-associated carbon and pH. The positive relation of organic carbon and nitrogen mineralisation with soil pH and total or particulate organic matter suggests that the pH-stimulated mineralisation of SOM mainly occurred in the particulate organic fraction (and not in the mineral–associated organic fraction) (Li et al., 2007).

The current thought on organic matter decomposition is that fungi-dominated decomposition occurs in undisturbed systems and bacteria-dominated decomposition in intensively managed systems (Bardgett and McAlister, 1999; Horwath, 2007). Fungi assimilate 30 – 40% of the carbon in plant litter into their biomass and bacteria 5 – 10%, leaving the remainder as CO_2 in the soil-atmosphere system (Crowley and Alvey, 2002). As a consequence a shift from fungi-dominated systems to bacteria dominated systems, resulted in a higher soil metabolic quotient ($troqCO_2$, see Box 2 for a description) and this in his turn may result in a smaller retention of SOM in bacteria-dominated systems than in fungi dominated systems. This happens e.g. at an increase of low soil pH's reducing the fungal respiration component (Crowley and Alvey, 2002).

Box 2

qCO_2 is the metabolic quotient or specific respiration rate, expressed as the amount respired per unit micro biomass and per unit time (mg C per g microorganism-C and per hour). It indicates the efficiency of the soil microbial biomass in utilising organic substances during biosynthesis (Aciego Pietri and Brookes, 2008a). An increase of qCO_2 indicates reduced substrate-use efficiency which may be related to stress (Li et al., 2007). It has been usually suggested as a more (than basal respiration) sensitive and effective indicator of microbial activity and soil quality, together with microbial quotient (Tian et al., 2008). According to Anderson and Domsch (1993), a high qCO_2 at a low pH can be an indicator of terrestrial microbial community stress, and accordingly little biomass can be produced because more carbon is used for respiration (Anderson, 2003).

3.1.2 Impacts on carbon mineralisation rates

In the experiment of Aciego Pietri and Brookes (2008a) mentioned in Chapter 1, the CO_2 production increased as pH increased with a tendency of stabilisation at pH values between about pH 5 – 7 (figure 5).

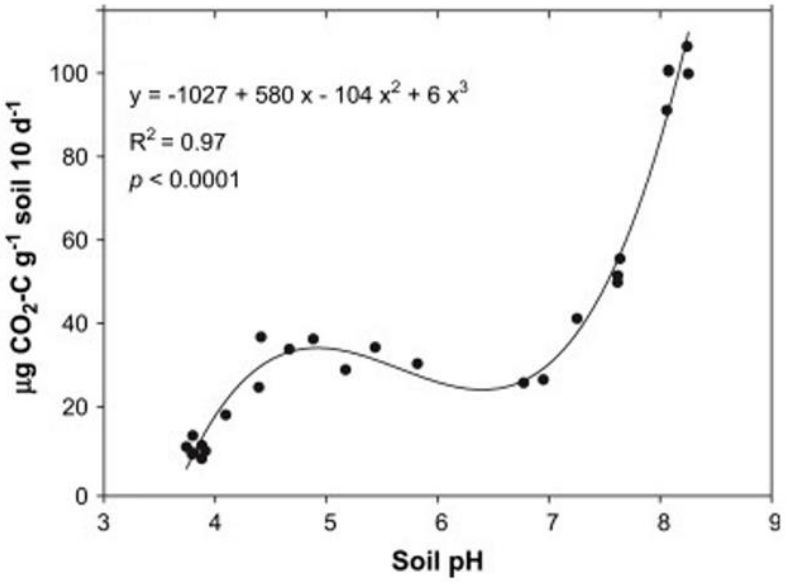

Figure 5 *Respiration (in µg CO_2-C g^{-1} 10 d^{-1}) as function of pH. From: Aciego Pietri and Brookes (2008a).*

At a low pH low CO_2 production is caused by toxicity stress (Al), at a high pH high production is caused by both high microbial activity and abiotic CO_2 production from $CaCO_3$. Reth et al. (2005) studied the respiration on bare soils, meadow soils and forest soils in Northern Germany. Soil temperature and soil water content appeared to be the most important factors influencing respiration. In addition, soil pH and root mass were important factors describing the spatial variation of respiration due to vegetation productivity and microbial activity spans. The pH appeared to be a major factor in regulating the carbon (and nitrogen) dynamics of agricultural soils as well (figure 6).

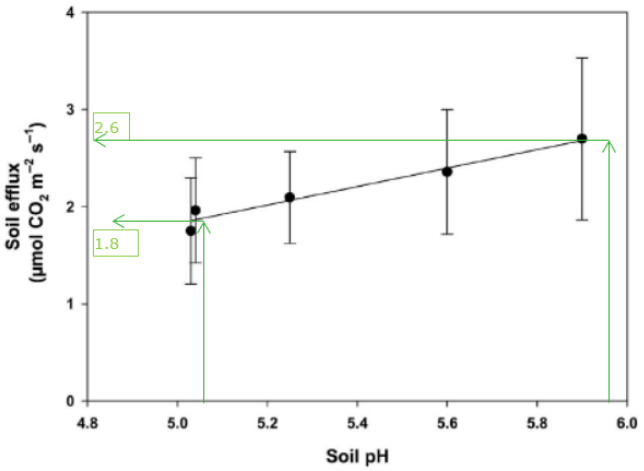

Figure 6 *Soil respiration (μg CO_2 m^{-2} s^{-1}) - mentioned here as soil CO_2 efflux - as function of soil pH-values. Dots represent the mean CO_2 fluxes (n = 5) with error bars. From: Reth et al. (2005).*

According to Kemmitt et al. (2006) there is a positive correlation between both plant productivity and intrinsic microbial respiration.

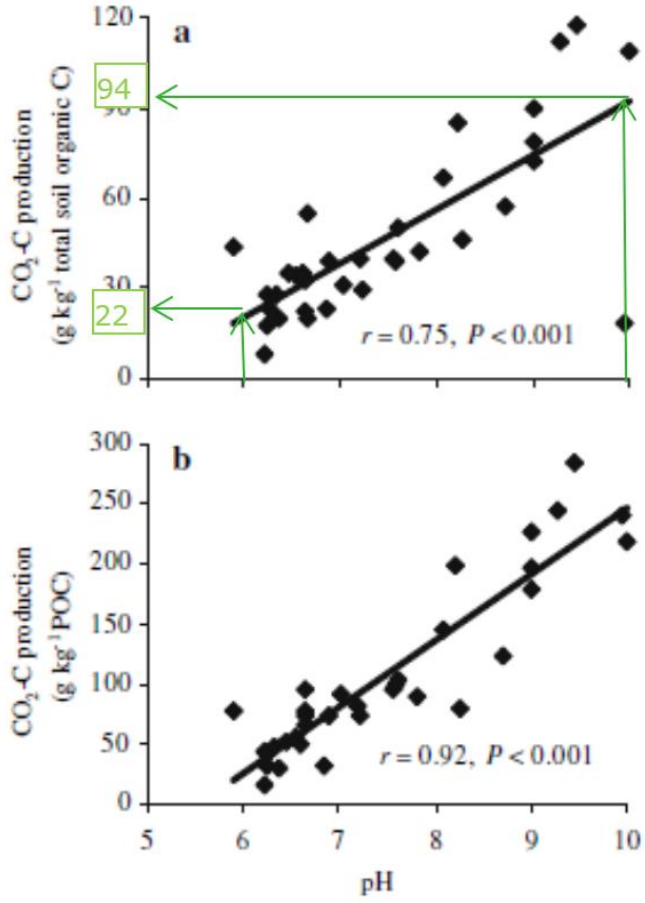

Figure 7 *Soil respiration expressed as g CO_2-C production per kg total organic carbon (a) or particulate organic carbon (b) over 90-day incubation. From: Li et al. (2007).*

Li et al. (2007)showed in their study - already mentioned in 2.3.4 – that the respiration was related to soil pH when expressed per kg of total organic carbon (figure 7a) and even more so when expressed per kg of particulate organic carbon (figure 7b), indicating that a major part of the pH-related improvement of carbon

mineralisation occurred in the particulate organic fraction. This result is in line with the result of Kemmitt et al. (2006) though expressed differently (figure 8). The qCO_2 also increased with an increase in soil pH, suggesting that increasing alkalinity favoured the survival of a bacterial-dominated community with low assimilation efficiency of organic carbon. As a result, a high amount of substrate carbon was lost from the soil as qCO_2 through increased respiration with increasing pH. The pH-stimulated mineralisation of organic matter (together with decreased plant productivity and litter input) was responsible for a decreased amount of organic matter in alkaline salt-affected sandy soils.

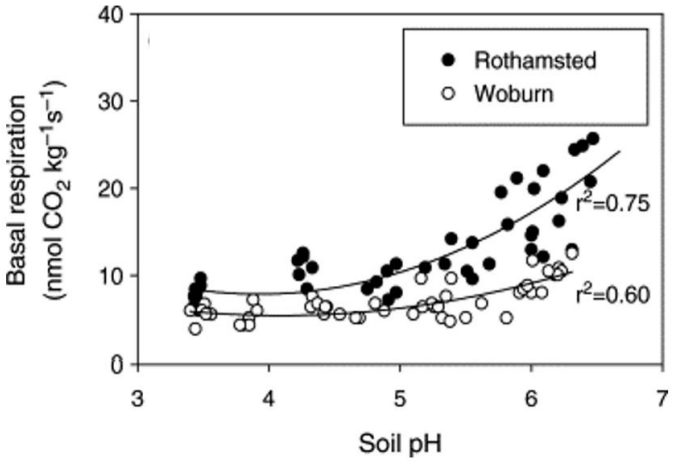

Figure 8 *Soil respiration expressed as nmol CO_2 per kg soil per second as function of pH. From: Kemmitt et al. (2006).*

Tian et al. (2008) investigated the microbial activity in a karst region in China. In this region soil pH showed a marked variation from 4.1 - 7.9. It appeared to be an important factor affecting soil microbial activity in terms of basal respiration rate (figure 9). Soil microbial activity, expressed as basal respiration, declined linearly with decreasing pH (depending on soil layer, figure 9). According to Tian et al. (2008), the changes in activity could in turn caused by changes in soil microbial community, also because of associated pH sensitivity and of carbon or nutrient-utilizing efficiency of the different microflora (Blagodatskaya and Anderson, 1998; Bååth and Anderson, 2003). They think that studies of the bacterial and fungal composition are necessary to interpret the mechanism of the effect of pH on microbial activity. Remarkably enough, DeLaune et al. (1981) noticed this already in 1981. Actually, they put the pH dependency of organic matter mineralisation in a wider perspective when stating: soil pH probably governs organic matter mineralisation by determining the kind, numbers and activity of microorganism involved in the mineralisation.

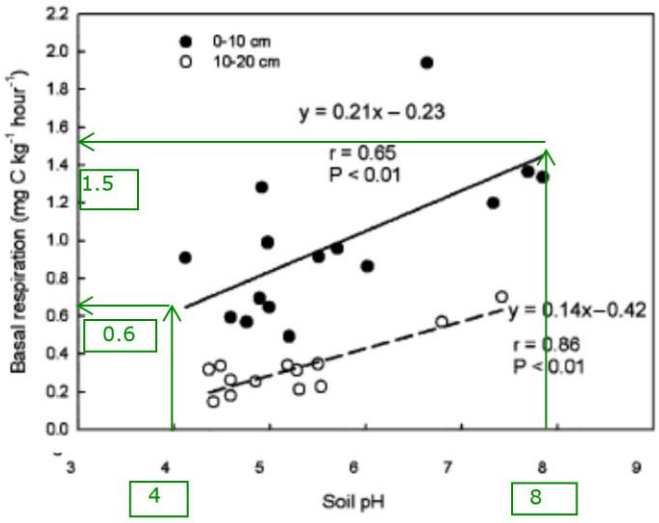

Figure 9 *Basal respiration rate (mg C kg^{-1} h^{-1}) as function of pH. From: Tian et al. (2008).*

Microbial communities from Fagus and Fagus-Quercus forest soils in Germany released more CO_2 per unit microbial biomass and time under acidic soil conditions (i.e. higher qCO_2) than communities under neutral conditions. By contrast, microbial quotients increased by increasing pH (Anderson and Domsch, 1993; Xu et al., 2017). The researchers postulate the occurrence of a high qCO_2 as an indicator of microbial community stress reflecting a higher maintenance requirement of the microbial community or a shift in the bacterial-fungal ratio. This is also taken up in the Handbook of Regel by Crowley and Alvey (2002).

Motavalli et al. (1995) observed that acidic soil pHs reduce decomposition rates of freshly–added organic material in tropical forest soils and the microbial biomass. They reported a linear relationship between organic carbon mineralisation and pH ranging from 3.9 and 6.7 in these soils. Soil acidity leads to a greater accumulation of SOM due to a reduced rate of microbial mineralisation.

In an arable field, respiration was not as strongly affected by pH between pH 8.3 and pH 4.5 (figure 10) as the microbial growth-rates were affected (figure 4a and 4b). The shift in fungal and bacterial importance along the pH gradient decreased the total carbon mineralisation, measured as basal respiration, by only of about 40% as calculated from (0.53-0.32)/0.53≈0.40 (data derived from figure 10).

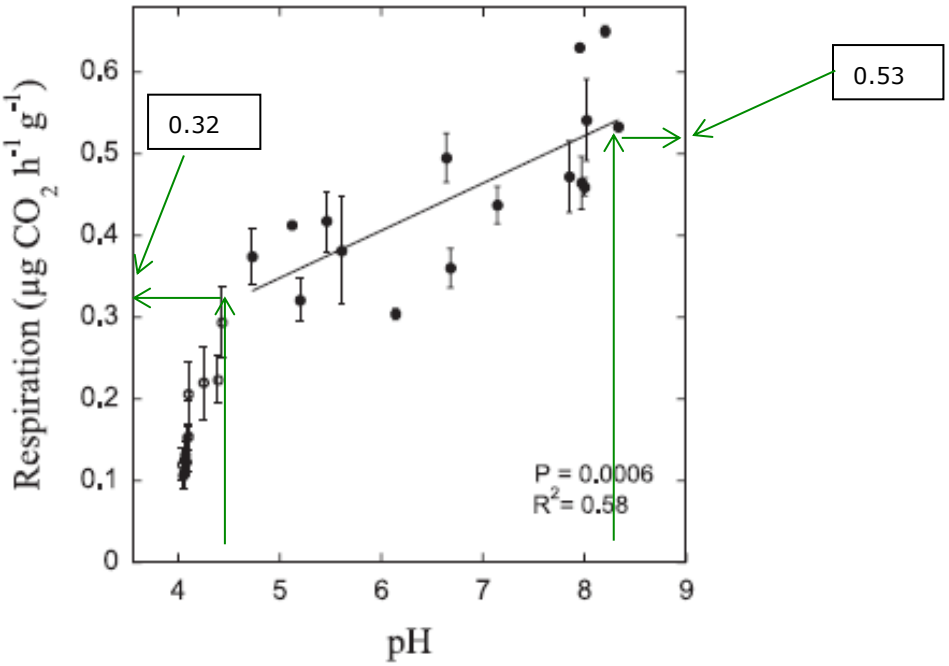

Figure 10 *Respiration (µg CO_2 h^{-1} g^{-1}) as function of pH. Data for pHs < 4.5 were not used in regression analysis. The error bars indicate+/- standard error (n=2). From: Rousk et al. (2009).*

This functional redundancy was also present in the grassland experiment of Rousk et al. (2011a): though in view of growth the relative importance of fungi increased by a factor of about 50 with decreasing pH, soil respiration decreased only by a factor of about 1.4 (1/0.7) (figure 11). They also observed a nearly linear increase of soil CO_2 emission between pH values of 3 and 7/8. It should be noted that this pH trajectory is somewhat wider than those used by Rousk et al. (2009) in their arable field experiment, and thepH - respiration relation showed a bend point around pH 4.5 (figure 10) which was absent in figure 11. In this context it should be kept in mind that the dimensions used for respiration are different; it is expected that this will not largely modify the general trend of respiration with pH (the conversion factors are constant along the experiment).

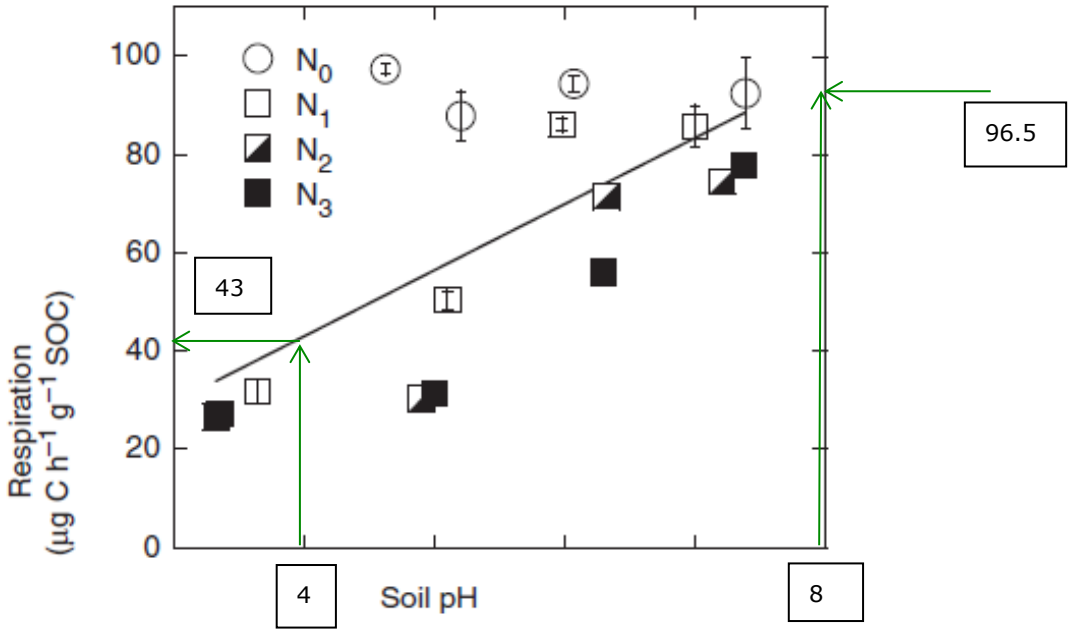

Figure 11 *Respiration (µg C h^{-1} g^{-1} soil organic carbon) as function of soil pH in the Park Grass soils. Curves are fitted to the average of the four nitrogen treatments, and are regressed against soil pH: 3 - 8. Symbols are coded according to the nitrogen fertilization treatments (N0, N1, N2 and N3 receiving 0, 48, 96, 144 kg $Nha^{-1}jr^{-1}$ resp.) and denote the mean (n=2) with error bars denoting ± 1 SE. SOC stands for soil organic carbon. From: Rousk et al. (2011a).*

Blagodatskaya and Anderson (1998) studied the effects of pH and substrate quality on the fungal-to-bacterial respiration ratio and qCO_2 of microbial communities in forest soils. They show that in general soil pH influenced the fungal-to-bacterial respiration ratio to a greater extent than the forest substrate type (the effect of pH was more pronounced under beech than under spruce, see table 2). This amounts to an increase of fungal respiratory activity and a decrease of bacterial respiratory activity under acidic conditions, a result seen before. Additionally, qCO_2 was 1.5-fold higher in low pH soils than in neutral ones. Soil pH strongly affected the qCO_2 while substrate quality did not have a significant influence on qCO_2. This points to a shift in the fungal-to-bacterial respiration ratio and possible also a higher maintenance carbon demand related to microbial community stress (Box 2).

Table 2 *Soil pH and substrate effect on fungal-to-bacterial respiration ratio and qCO_2. Substrate: beech or spruce, low pH: 3, high pH: 6. From: Blagodatskaya and Anderson (1998).*

Soil pH and substrate	fungal-to-bacterial respiration ratio	qCO_2 (µg qCO_2-C mg^{-1} C_{min} h^{-1})
Beech, pH 3	18.2	1.9
Beech, pH 6	3.0	1.6
Spruce, pH 3	9.5	2.4
Spruce, pH 6	5.6	1.3

3.2 Impacts of pH on nitrogen mineralisation

Nitrogen is the second most important element in the mineralisation of organic matter. Nitrogen mineralisation is linked to carbon mineralisation by C/N of the specific organic compound to mineralise (litter). Both substrate availability and C/N of the soil influence nitrogen mineralisation rates. These effects translate into characteristic differences in nitrogen cycling among ecosystem types (Booth et al., 2005); C/N can be considered as a key indicator. The amount of nitrogen that will release into the soil might differ from that of carbon due the importance of the C/N of the microorganisms in this respect: if C/N of the

microorganisms deviate from C/N of the litter, only part of the nitrogen of this compound will be immobilised and will benefit plant growth and development.

This paragraph is dealing with the effect of pH on nitrogen mineralisation or how these process rates change with pH and is split up in three parts. The first part is about the first step (ammonification) and the second part about the second step (nitrification) in the nitrogen mineralisation process. While these two parts gives general and more qualitative remarks, the third part explicitly gives the quantitative relationships of both ammonification and nitrification as discovered from field observations or lab experiments. As the effects of pH on these processes follow on from they are treated within one paragraph.

3.2.1 Impacts on nitrogen mineralisation processes

In this section we describe the impacts of pH on both ammonification, being equal to mineralisation of organic nitrogen to ammonium and nitrification, being the transfer of ammonium to nitrate.

Ammonification: general remarks
Nitrogen mineralisation, also referred to as ammonification, is the transformation of organic nitrogen compounds into ammonia. This process occurs under aerobic conditions by heterotrophic microorganisms. Ammonification is preceded by proteolysis (the enzymatic breakdown of proteins with aid of proteolysis enzymes, leading to amino acids). The reaction equation of ammonification reads:

$R\text{-}NH_2 \rightarrow NH_4^+ + R^-$

In the process of nitrogen transformation, ammonification is generally insensitive to pH and can be measured at significant rates over a wide pH range; ammonification is still active at around pH 4 and around 8 (Harmsen and van Schreven, 1955; Fu et al., 1987). However, according to Kemmitt et al. (2006) ammonification is greatly suppressed with increasing pH and Wood (1988) and Paul and Clark (1989) give a smaller optimum range soil pH 6.0-8.0. In this sense it is highly comparable with the carbon mineralisation described above. According to Falkengren-Grerup et al. (1998) and Fu et al. (1987), pH is a factor of major importance for nitrogen mineralisation as found in deciduous forest soils in Sweden, and nitrification as found in both untreated and crop-residue-treated soils in Iowa. Besides the pH, they also show the importance of organic matter composition as well soil chemical and physical factors in this respect. These references show that the magnitude of pH importance might differ between experiments/natural environments: actually a demonstration of the complexity of factors that influence into some extent the mineralisation.

According to Alef and Kleiner (1987) arginine ammonification is an alternative expression of microbial activity (i.e. nitrogen mineralisation) in soils as proteins and amino acids comprise an important input of organic nitrogen into soil systems and are a major precursor of ammonium production. In this case arginine, added to a soil in an incubation experiment, was used as an organic nitrogen substrate. Aciego Pietri and Brookes (2008b) report weak or no relationships between soil pH and arginine ammonification when soils with different pHs but also varying in other factors, were used. These factors confound the real pH effect on mineralisation.

Nitrification: general remarks
The process of conversion of ammonia into nitrite and then into nitrate is called nitrification. Nitrification is preceded by ammonification. In this context, a difference has to be made between autotrophic and heterotrophic nitrification. Autotrophic nitrifiers always acquire energy by nitrification while heterotrophic ones do not (Zhu et al., 2013). This will be elaborated below.

Autotrophic nitrification

Autotrophic nitrification is an aerobic process by autotrophic bacteria. In this case ammonia and nitrite are used as electron donors for metabolism; both inorganic molecules function as energy source and so are linked to microbial growth. Nitrification, at neutral pH, consists of two steps: oxidation of ammonia to nitrite and oxidation of nitrite to nitrate (Agriinfo, 2012; Amoo and Babalola, 2017; Schlesinger and Bernhardt, 2020) and are given with the accompanying reaction equations:

Ammonia oxidation to nitrite [1)]:	$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$	(1)
Oxidation to nitrate:	$2NO_2^- + O_2 \rightarrow 2NO_3^-$	(2)
Total reaction:	$2NH_3 + 4O_2 \rightarrow 2H^+ + 2NO_3^- + 2H_2O$	(3)

[1)] In this process hydroxylamine (NH_2OH) is an intermediate product.

An important characteristic of the first step is the production of acidity (Olness, 1999). This production of acidity leads to a decline in nitrogen mineralisation as the microbial biomass diminishes at low pH (they grow best at neutral pH) (Crowley and Alvey, 2002; Myrold, 2005), an intrinsic negative feedback: it enhances the ammonia oxidation to nitrite (also called nitrosification) rate in soil systems with pH larger than optimum and it inhibits this rate in soil systems with pH smaller than optimum (Amoo and Babalola, 2017).

Ammonium oxidisers are distinguished by the prefix Nitroso for the genus name and the nitrite oxidisers by the prefix Nitro (Tate, 2000). The last step is also possible by several fungi and actinomycetes (Agriinfo, 2012). Nitrification is reported to be performed by both acid-tolerant and acid-sensitive nitrifiers (De Boer et al., 1990). This limited number of bacterial species involved in these processes forms a major contrast with both carbon and nitrogen mineralisation, where a wide diversity of soil microorganisms are involved (Tate, 2000).

The oxidation to nitrate can be divided in two steps: the oxidation of nitrite into nitrate with the aid of nitrite oxidoreductase, and the conversion of electrons, free hydrogen ions and oxygen into water. Nitrite oxidoreductase is found in nitrite-oxidising bacteria (De Boer and Kowalchuk, 2001; Amoo and Babalola, 2017; Fu et al., 2020; Ayiti and Babalola, 2022).

Numerous microorganisms can oxidize ammonia. These microorganisms include bacteria, archaea and even fungi. The ammonia-oxidizing bacteria entail the genera Nitrosomonas, Nitrosospira and Nitrosococcus. Fungi that can oxidize ammonia are Aspergillus flavus, Penicillium and Absidia cylindrospora (Zhu et al., 2015; Amoo and Babalola, 2017). More information can be found in Prosser and Nicol (2012).

Ammonia oxidizing archaea occur mainly in acidic/neutral soils and ammonia oxidizing bacteria in neutral/alkaline soils. Neutral soils are more sensitive to pH induced changes in nitrification than acid or alkaline soils. This increased sensitiveness is related to substrate competition between the archaea and bacteria. The abundance of these archaea / bacteria strongly affects the nitrification in neutral soils. Fungi commonly thrive more than bacteria in an acidic soils (Amoo and Babalola, 2017; Wang et al., 2019). More information can be found in Zhang et al. (2012).

Principally, both archaea and bacteria are responsible for ammonia oxidation in acid soils as was observed in an acidic subtropical pine forest soil and the autotrophic nitrification dominated over heterotrophic nitrification (Faeflen et al., 2016). Generally, the archaea generally have a larger contribution than the bacteria in acidic soils, although some acid-tolerant acidophilic bacteria can also contribute to ammonia oxidation. Remarkably enough, in a highly-acidic tea plantation, soil specific acidophilic archaea adapted to grow at low pH, dominate over the bacteria. Some archaea in acidic soils are ureolytic and can directly generate ammonia from urea, a mechanism to cope with ammonia shortages in these soils (De Boer and Kowalchuk, 2001; Li et al., 2018). In addition, autotrophic nitrification is limited in forest peat deposits in Canada (Westbrook et al., 2006). It all shows that effects of pH on nitrification are not straightforward. See also Maslov et al. (2022).

In comparison to the amount/abundance of ammonia oxidizing microorganisms, the amount/abundance of microorganism that can oxidize nitrite is somewhat more restricted, even uncertain (Fu et al., 2020). Therefore, the ammonia oxidation is usually considered to be the rate-limiting step in nitrification (Kowalchuk and Stephen, 2001); see also above. Nitrite oxidizing bacteria include the genera Nitrobacter and Nitrospira. Their

occurrence/activity is the highest in alkaline soils (they occur mainly in alkaline soils) (Wang et al., 2019). Notably, Nitrospira include some species that contain ammonia monooxygenase and can undertake complete nitrification, converting ammonia to nitrate of are capable to completely oxidize ammonia to nitrate (the comammox process, a compilation the words 'complete' and 'ammonia' (Daims et al., 2015; Pjevac et al., 2017).

Nitrification is strongly affected by soil pH (Cheng et al., 2013). A pH increase accompanies with an increase in ammonia availability, the substrate of nitrification (Burton and Prosser, 2001). Hence, it was originally assumed that nitrification is absent in highly acidic soils (De Boer and Kowalchuk, 2001). Besides a reduction in the ammonia availability, also the abundance and activity of ammonia oxidizers are reduced (Daims et al., 2015). Since nitrification is more restricted to optimal pH conditions than ammonification is, accumulation of ammonium is the result at both too low and too high pH and so liming increased nitrification more than ammonification, thereby increasing the nitrate content and not the ammonium content (Harmsen and van Schreven, 1955). Fu et al. (1987) observed that most of the mineral nitrogen produced under neutral or slightly alkaline conditions was in the form of nitrate, indicating that nitrification is considerably enhanced at high pH values, while ammonium was detected only at pH 4. The conversion of ammonium to nitrate by ammonia oxidising and nitrite oxidising bacteria respectively occurs at the fastest rate in slightly alkaline pH soils. In this context, three general patterns exist (Crowley and Alvey, 2002):

- 6.9 < pH < 7.8 : nitrite accumulation;
- 5.0 < pH < 6.4 : no nitrite accumulation;
- pH < 5.4 : slow oxidation of ammonium to nitrate.

The nitrifying bacteria, have a rather narrow pH optimum: ammonium conversion to nitrate occurs most rapidly at pH 6.9 - 7.8 (Wood, 1988) and Paul and Clark (1989) give as optimum soil pH 7.5-8.0), with an accumulation of nitrite because ammonium oxidation is faster than nitrite oxidation (Harmsen and van Schreven, 1955). This results from the fact that ammonia is toxic to Nitrobacter (Tate, 2000). As under alkaline conditions (pH 6.9-7.8) nitrite oxidisers are inhibited while ammonium oxidisers remain active, nitrite will accumulate. Between pH 5 and 6.4 the oxidation of ammonium is slower than under alkaline conditions and nitrite does not accumulate. At pH < 5.4 however, this conversion of ammonium is very slow and ammonium will accumulate (Tate, 2000; Crowley and Alvey, 2002).

Increase in soil pH by soil liming stimulate the soil nitrifying activity (or net nitrification rate) in acid forest soils (Carnol et al., 2002; Bäckman et al., 2003; Nugroho et al., 2007). An example of the stimulating effect of liming on nitrification in an experimental crop field experiment is given in figure 12. However, Hayatsu et al. (1993); Yao et al. (2011) found that liming decreases this activity in a highly acid tea plantations. These contrasting results indicate that other effects besides substrate availability are likely involved in influencing the process of nitrification (Wang et al., 2019).

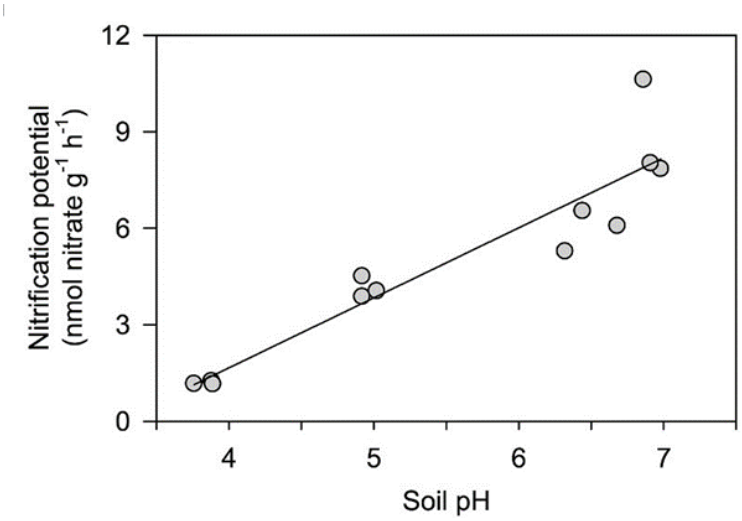

Figure 12 *Nitrification potential (nmol nitrate g^{-1} h^{-1}) as function of soil pH. From: Abalos et al. (2020).*

Keen and Prosser (1987) gave an additional explanation of the pH dependent behaviour of nitrite oxidation: competitive inhibition between OH^- and NO_2^- at high pH and inhibition by free nitrous acid at low pH. According to Falkengren-Grerup et al. (1998) and Myrold (2005) this last value is 4.5, and according to Persson and Wirén (1995) 4. At pH < 4 the population size of ammonia oxidising bacteria in acidic forest is below detection (Klemedtsson et al., 1999; Booth et al., 2005) and Tate (2000) suggested that nitrification occurs primarily in soils with pH > 5.5 because nitrification is catalysed primarily by a small group of autotrophic bacterial species that are pH sensitive. The incubations results of Tian et al. (2013) with forest soils in a karst region of China delivered the same critical pH point for nitrification. In another study the maximum conversion to nitrate was at pH 6.7 and negligible at pH < 5 and pH > 8.5 (Olness, 1999) with a nearly symmetrical relationship in between (Olness et al., 2001), values reasonably comparable to those mentioned by Crowley and Alvey (2002). Also Ayiti and Babalola (2022) mention pH 5 as limit value for nitrification and (Sahrawat, 2008) pH 5.5 as limit value and pH 8 as optimal pH. Viewed globally, the net N mineralisation rates decrease with the soil pH (Li et al., 2019) and this also holds regionally (Wang et al., 2019). According to Le Moal et al. (2019) ammonia oxidation is inhibited at pH 5 while nitrite oxidation is inhibited at pH 8.5 and the optimal pH's are respectively 7.5 and 7. The values given apparently show that they are not fixed and that after high probability other factors interfere with pH in the nitrogen transformations. In addition, Olness (1999) made the noticeable remark that variation observed in the natural nitrate production in the US Cornbelt study seems explained by a complex effect of H^+ and OH^- on microbial activity and subsequent nitrification. According to Li et al. (2020) the given negative relationship between nitrification and pH is caused by two reasons. First, a lower pH reduces the biomass (richness and diversity) of autotrophic bacteria and archaea (Aciego Pietri and Brookes, 2008b; Hu et al., 2013) as well their microbial activity (Nicol et al., 2008; Zhang et al., 2017) Second, a lower pH provides less organic substrate for the soil nitrification (Wang and Chen, 2012).

The kinetics and occurrence of nitrification in soil reflect that a limited number of bacterial species are involved in this process. According to Tate (2000) the primary concerns in predicting the extent and rate of nitrification in an ecosystems are the substrate availability, temperature, pH, oxygen tension and soil moisture. A typical example of the influence of soil moisture in this respect concerns the periodic soil moisture fluctuations in peat soils. According to Fierer and Schimel (2002) these fluctuations have a direct effect on the microbial community and so on the abundance and functioning of nitrifiers. Additionally, both metal contamination and salinity have been demonstrated to have significant impact on nitrification rates.

Myrold (2005) presents a decision tree of factors involved in regulating nitrification in a soil with the most important factors on top of this tree (figure 13). If all factors are favourable, nitrification is likely to occur, and if any factor is unfavourable it is unlikely. Though nitrifiers are present in most soils, exceptions exists. Persson and Wirén (1995) have discovered that a lack in nitrate formation could have been due to the absence of nitrifiers: addition of $CaCO_3$ to a humus sample did not result in any nitrification. Liming in the absence of fertilizer nitrogen stimulated microbial activity but depressed the net nitrogen mineralisation due to immobilisation (Williams, 1972). Nitrogen fertilisation or increasing the availability of ammonium often gradually increases the nitrifier populations and the nitrification rates until they reach a new and higher steady state. Fertilisers in general might be expected to stimulate microbial activity in SOM either directly, by adding nutrient elements that may be in short supply, or indirectly by modifying pH, ion-exchange properties and other indicators of the physico-chemical environment of the soil (Williams, 1972). So, as Tate (2000) also states, changes in the nitrification rate are dependent upon the capacity of the nitrifiers population density to increase. In addition, dependent on the presence of different groups of nitrifiers (autotrophic and heterotrophic, and acid-tolerant and acid-sensitive nitrifiers, see before), nitrification can vary between sites and within a soil profile (Falkengren-Grerup et al., 1998). Persson and Wirén (1995) have observed that nitrification was sometimes low despite a favourable pH, indicating that other factors than pH might have restricted nitrification. Apparently another factor might overrule the pH.

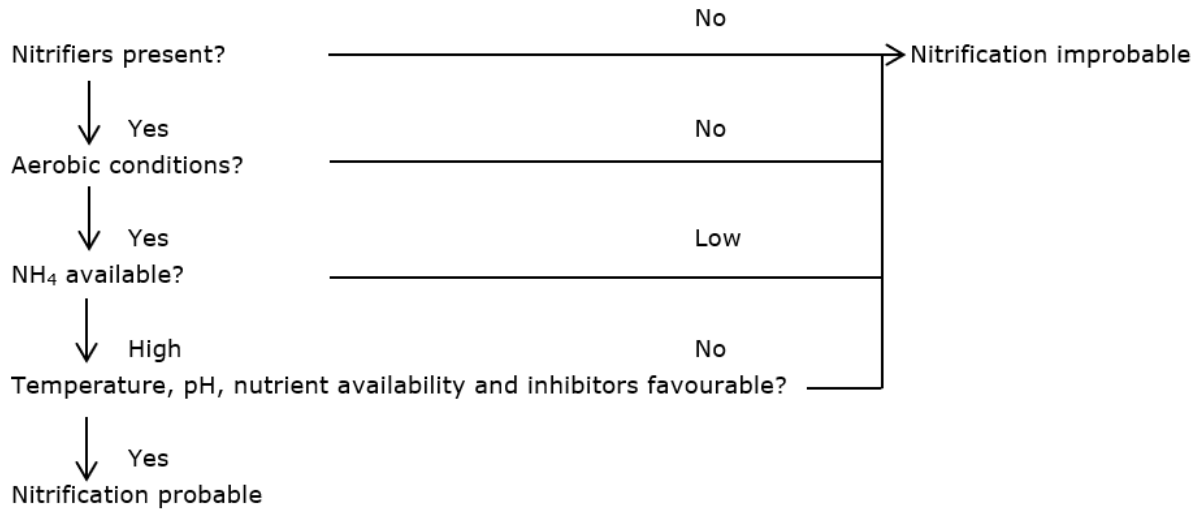

Figure 13 *Decision tree of factors regulating nitrification in soil.*

As opposed to Myrold (2005), Tate (2000) as well as Booth et al. (2005) and Robertson and Groffman (2007) state that the *single* most important factor regulating nitrification in the majority of soils is the ammonium supply and may have two causes. First, the usually low concentrations of ammonium and nitrite in soils and second the acceleration of nitrification usually only occurring when ammonium supply exceeds plant and heterotroph demand. This last statement shows that nitrifiers are poor competitors for ammonium. Thus, it appears that it is still unclear which factor controls nitrification.

Nitrification activities are often low in soils at pH < 4.5, especially in agricultural soils. Autotrophic nitrifiers are generally thought to be neutrophilic. Nevertheless, high nitrification rates or high nitrate concentrations have been observed in many acid soils (pH <4.5) (Tate, 2000; Myrold, 2005; Aciego Pietri and Brookes, 2008b). Nitrification may even occur in extremely acidic soils (De Boer and Kowalchuk, 2001; Bergamasco et al., 2019). According to Tate (2000) and De Boer and Kowalchuk (2001) several explanations exist: 1) the existence of acidophilic autotrophic, 2) heterotrophic nitrifiers and 3) the occurrence of alkaline microsites in otherwise acidic soils. It is not clear which explanation actually holds: acidophilic autotrophic may exist, heterotrophic nitrifiers are present and microsites of higher pH are plausible, either associated with reactive surfaces or created by the activity of microorganisms themselves. For example, ammonia released during mineralisation of organic nitrogen by heterotrophs or from urea hydrolysis may alter microsite pH (Myrold, 2005). Tate (2000) and De Boer and Kowalchuk (2001) also mention that adaptation of the growth properties of commonly encountered nitrifier populations could accommodate these acidic conditions. According to Robertson and Groffman (2007) however, in acid soils most nitrification is autotrophic and not heterotrophic as previously thought, although the exact mechanisms by which nitrification occurs at low pH are not well understood. Heterotrophic nitrification thus appears important in some soils and microenvironments, perhaps particularly where autotrophic nitrifiers are chemically inhibited, but are now thought to rarely dominate the soil nitrifier community. Though low soil pH does not exclude nitrification in vegetated soils, yet also many acid soils exist where nitrification is absent (Robertson, 1982).

Heterotrophic versus autotrophic nitrification

While ammonia oxidisers are strict autotrophs, nitrite oxidisers are capable of heterotrophic growth under some limited circumstances. Heterotrophic growth by nitrite oxidisers is much slower than other heterotrophic bacteria and slower than autotrophic nitrite oxidisers. So, heterotrophic bacteria grow slowest of all three bacterial groups. Examples of heterotrophic nitrifiers are the fungi Aspergillus and Penicillium and the bacteria Arthrobacter and Paracoccus (Zhang et al., 2020). To complete and even to complicate the picture, a wide variety of heterotrophic bacteria and fungi exists that oxidise either ammonium or organic nitrogen to nitrite or nitrate (also called heterotrophic nitrification) (Li et al., 2018). The oxidation via both the inorganic (^{15}N-NH_4^+) and the organic pathway (^{15}N-Glycine) is well illustrated in figure 14. These heterotrophic microorganisms or heterotrophic nitrifiers gain, unlike autotrophic nitrifiers, no energy through this activity and so it is not linked to cellular growth. The quantities of nitrite and nitrate produced by the heterotrophic nitrifiers are small compared to those produced by the autotrophic nitrifiers (Faeflen et al.,

2016). Though the relative importance of these nitrifiers is still debated, autotrophic nitrifiers often dominate nitrification activity in most soils. Because autotrophic nitrifiers often dominate nitrification activity, it is possible that CO_2 concentrations may also influence the growth of nitrifiers. This CO_2 fixation has been recently proven for the thauma ammonia-oxidizing archaea (Zhang et al., 2020). Due to their low growth rate and relatively inefficient metabolism, autotrophic nitrifiers are thought to be more sensitive to temperature than common heterotrophs (Tate, 2000; De Boer and Kowalchuk, 2001; Myrold, 2005; Robertson and Groffman, 2007; Zhang et al., 2023).

In acidic environments unfavourable for autotrophic nitrifying bacteria, nitrification may result from the activity of heterotrophic bacteria/fungi (Brierley and Wood, 2001), since ammonia oxidizers are poor competitors for ammonium relative to ammonia-assimilation heterotrophic bacteria/fungi when ammonium is limited (van Niel et al., 1993; Verhagen et al., 1995). This can be generalised as: heterotrophic nitrification is important in specific environments (e.g. high temperature, high alkalinity, lack of oxygen and nutrition) that are not conducive to autotrophic nitrification (Zhang et al., 2023). An example of the lack of nutrients are nitrogen-limited systems, especially natural forest soils where heterotrophic nitrifiers are potential contributors to nitrification (Li et al., 2018).

In acidic soils, organic nitrogen rather than mineral nitrogen is more favourable for the heterotrophic nitrifiers (Zhang et al., 2014; Zhang et al., 2020), as is shown in figure 14 and figure 15. Thus pH regulates the heterotrophic nitrification. Moreover, soil carbon content and the C/N interact with soil pH and correlate positively with heterotrophic nitrification. Hence, the activities underlying soil pH for heterotrophic nitrification may be covered by an effect of the carbon and nitrogen content of the soil (Zhang et al., 2020). According to Maslov et al. (2022) the carbon content and the enrichment of organic matter with nitrogen (C/N) are the most important limiting factors of heterotrophic nitrification. A high C/N stimulates the heterotrophic nitrifying activity of a soil as a result of a higher bioavailability or organic carbon, favouring the growth of fungi and heterotrophic bacteria, thereby limiting the growth and activity of autotrophic nitrifiers (Amoo and Babalola, 2017). According to Xiao et al. (2021) this favourable effect stems from the large competition on substrate (N or C) between those nitrifying groups. The availability of a limited range of substrates is a significant feature controlling heterotrophic nitrification (Zhang et al., 2014). Another reason may be the competition on ammonium at low dissolved oxygen levels (van Niel et al., 1993).

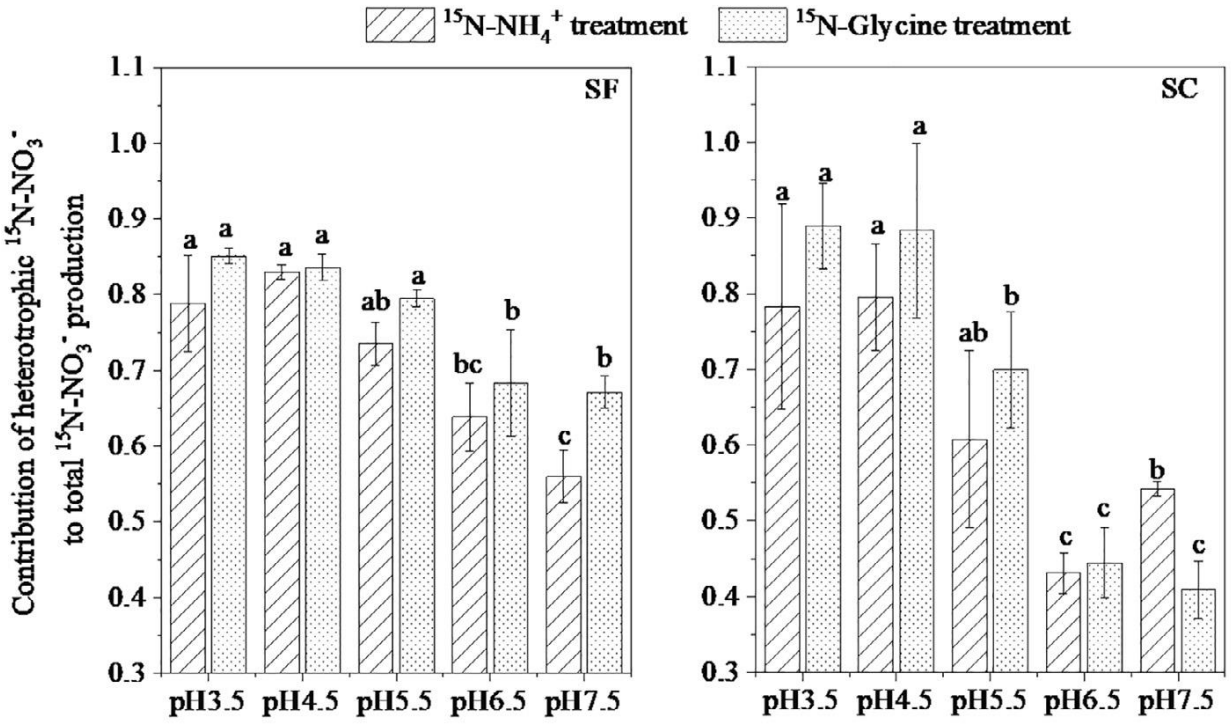

Figure 14 *The contribution as function of pH of heterotrophic ^{15}N-NO_3^- to total ^{15}N-NO_3^- production in the $_{15}N$-NH_4^+ and $_{15}N$-Glycine treatments in SF (forest soil) and SC (cropland soil). Identical letter means no significant difference in group ($p > 0.05$). From: Zhang et al. (2020).*

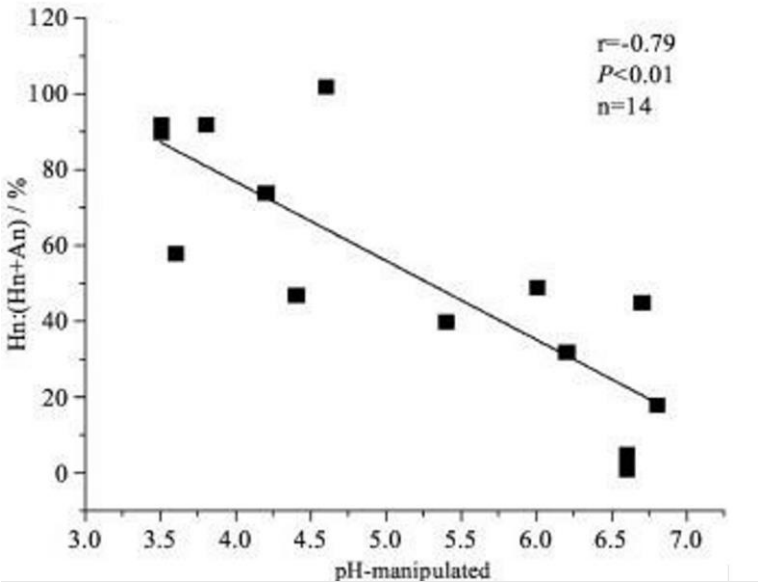

Figure 15 *The influence of pH on the contribution of heterotrophic nitrification (Hn) to the total nitrification (sum of heterotrophic and autotrophic nitrification; Hn+An). From: Zhang et al. (2023).*

While the previous paragraph considers heterotrophic nitrification from the heterotrophic point of view, this paragraph does this from the autotrophic point of view. There is evidence for two pathways of heterotrophic ammonia oxidation. The first one is similar to that of autotrophic oxidation. The second is organic and appears limited to fungi. The associated reactions are not coupled to ATP and thus produce no energy. Nitrification can occur in soils even at pH 3 (De Boer and Kowalchuk, 2001). Heterotrophic nitrification by fungi is inhibited at high pH because the involved fungi can occur under acidic conditions but prefer these conditions (Zhu et al., 2013; Zhang et al., 2015). Zhang et al. (2015) discovered a pH threshold for heterotrophic nitrification in soils from forest, grassland and arable land. Fungi are more efficient in (heterotrophic) nitrification than the bacterial counterparts as they are more acid-tolerant (Zhang et al., 2020). Hence they are the dominant heterotrophic nitrifiers in acidic soils (Zhang et al., 2020). However, in acid soils most nitrification is autotrophic and not heterotrophic as previously thought (De Boer and Kowalchuk, 2001), although the exact mechanisms by which nitrification occurs at low pH are not well understood. Analogously, Faeflen et al. (2016) have discovered that autotrophic nitrification is the main nitrification pathway in a subtropical pine forest soil (and not autotrophic nitrification). The same holds for a Scots pine forest soils (see Faeflen et al., 2016), while the reverse holds for a subtropical soil in China (Zhang et al., 2011). Heterotrophic nitrification thus appears important in some, particularly where autotrophic nitrifiers are chemically inhibited as seen in the previous paragraph, but are now thought to rarely dominate the soil nitrifier community (Robertson and Groffman, 2007).

Ammonia-oxidizing archaea and bacteria can produce N_2O by the so-called nitrifier denitrification process (Wrage-Mönnig et al., 2018). Liming acidic soils may increase this production by favouring ammonia-oxidizing bacteria over ammonia oxidizing archaea, since these bacteria have a higher production of N_2O per mole of ammonium than these archaea (Hink et al., 2017). In addition, some heterotrophic nitrifiers can nitrify and denitrify simultaneously. N_2O can also be generated by spontaneous decomposition of hydroxylamine and this process occurs in acid soils (Heil et al., 2016). Denitrification results in little or no nitrate accumulation in the soil (Matheson et al., 2003). Liming, however, can also decrease the N_2O production by continued/increased N_2O reduction via denitrification and by stimulating plant growth (Abalos et al., 2020) as shown in figure 16.

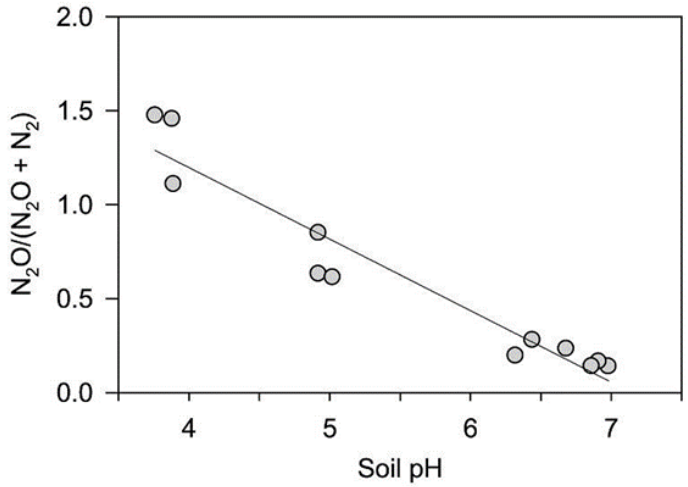

Figure 16 *$N_2O/(N_2O + N_2)$ ratio as function of soil pH. From: Abalos et al. (2020).*

3.2.2 Impacts on nitrogen mineralisation rates

In this section we describe the impacts of pH on ammonification and nitrification rates. A study by Falkengren-Grerup et al. (1998) showed that nitrogen deposition increases the rate of both mineralisation and nitrification. At high nitrogen loads (present in southern Sweden) with high soil N levels especially the most acidic soils doubled mineralisation rates. The nitrogen pool as well as the organic matter input changed in quality and in decomposability thereby favouring the ammonification. Thus, nitrification can increase because the substrate for the nitrifiers is not a limiting factor under such conditions. Probably the adaptation of the nitrifiers or changes in the microbial community in acidified soils do also a play a role in the increase of nitrification.

The results of the study of Falkengren-Grerup et al. (1998) are summarised in figure 17. The total inorganic nitrogen content, for all regions as a whole, was slightly negatively related to pH (figure 17 top left). Because of the high rate of nitrification, the sum of ammonium and nitrate is also a good indicator of the mineralisation. The amount of mineralised ammonium not transformed to nitrate was highest at pH < 4 and was almost absent at pH > 5. The corresponding production rate was negatively related to pH (figure 17 top right). Nitrification rates show an optimum behaviour with regard to pH (pH optimum around 4.3; figure 17 bottom left). At pH > 5 the nitrification ratio - the percentage of nitrate obtained at the end of the experiment involving ammonium plus nitrate - was nearly 100% (figure 17 bottom right), showing that almost all ammonium has been converted to nitrate. These results deviate from those of Klemedtsson et al. (1999), Olness (1999) and Tate (2000), expressing the overwhelming effect of nitrogen deposition over the soil pH effect: due to nitrogen deposition the pH above which nitrification occurs lowered unto around pH 3.5. Also from Booth et al. (2005) it becomes clear that nitrification is possible at pH < 5 when high soil nitrogen mineralisation rates occur.

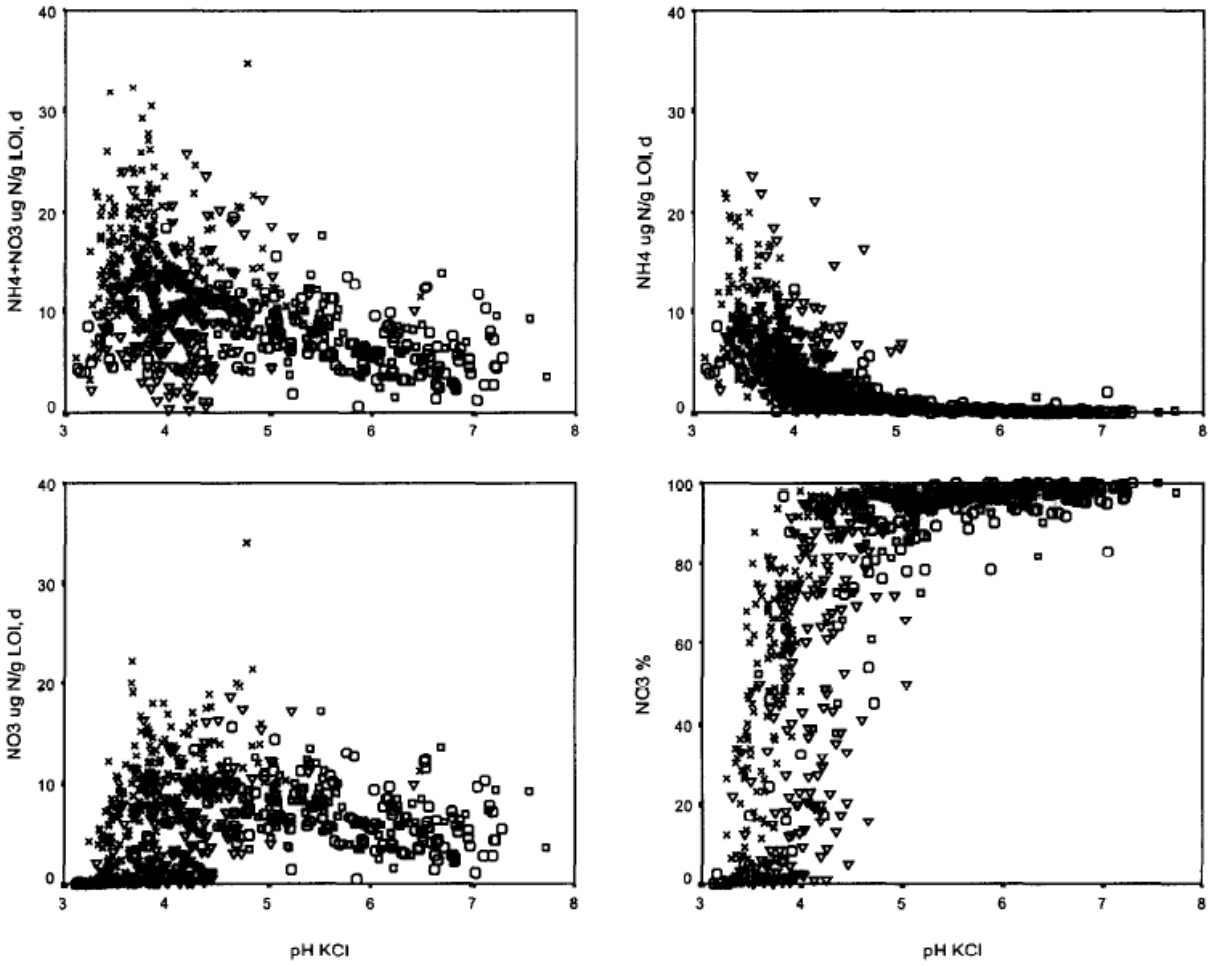

Figure 17 *Net nitrogen mineralisation and nitrification rate in relation to pH for four regions. Rates (µg N g^{-1}LOI d^{-1}) are given as (top left) total inorganic nitrogen (NH_4 + NO_3), (top right) ammonium (NH_4), (bottom left) nitrate (NO_3) and (bottom right) nitrification ratio (NO_3 %). (LOI refers to 'loss on ignition', and symbols refer to the different regions.) From: Falkengren-Grerup et al. (1998).*

Figure 17 top right and bottom left have been schematized by drawing a line to the centre of the clouds. This result is given in figure 18.

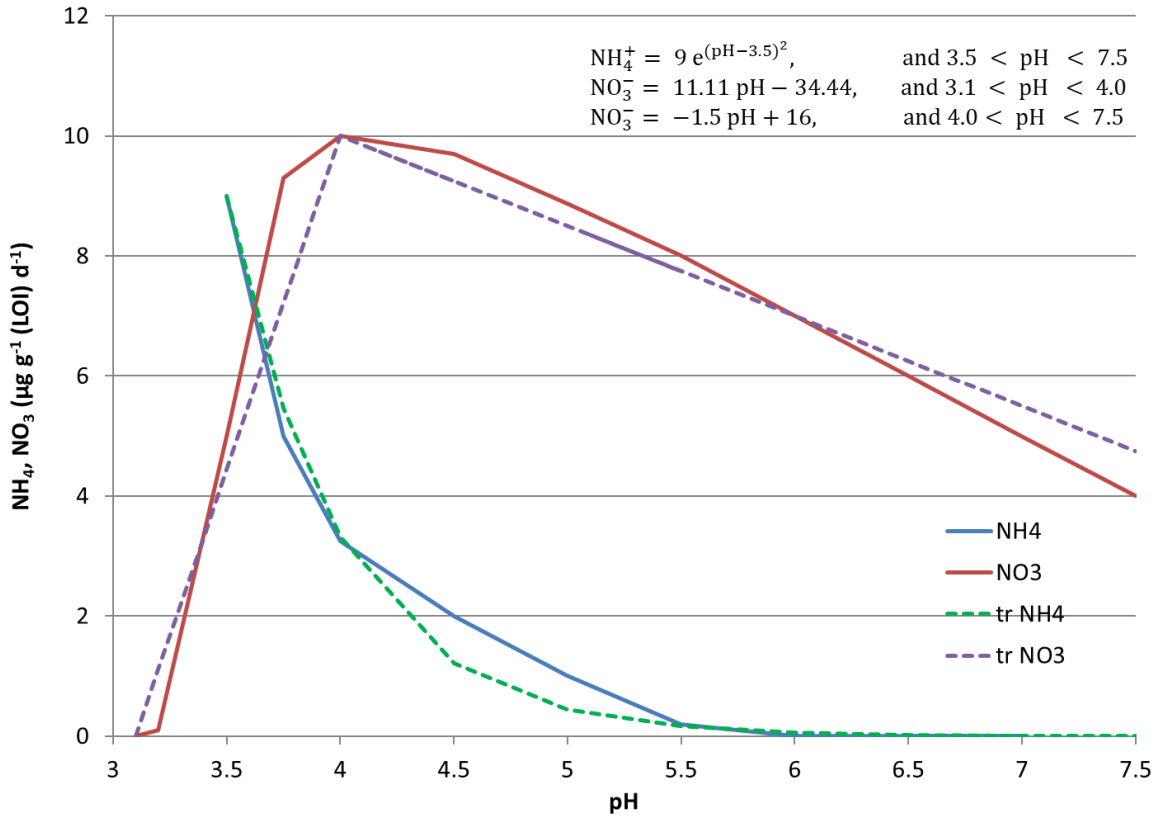

Figure 18 *Schematization of the net production of NH_4 + NO_3 (µg g^{-1} LOI d^{-1}) due to nitrogen mineralisation and nitrification rate as function of the pH based on figures 17 top right and bottom left.*

Aciego Pietri and Brookes (2008b) (already mentioned in paragraph 2.2.1 and 2.3.3 respectively) showed that ammonium concentrations decrease with increasing in control soils with native organic N.

While at low soil pH (around 3.7) nitrification is inhibited but not stopped, nitrification rate increases as soil pH increases up to about pH 8. Therefore, around pH 5, nitrification is rapid enough to prevent accumulation of ammonium. Crowley and Alvey (2002) found a similar boundary pH value. The accumulation of nitrate at low pHs and the nitrate concentrations were negatively correlated with increasing soil pH. To investigate these unexpected results, arginine was added as a labile source of organic nitrogen and its extent of ammonification and nitrification were measured at different pHs. Results obtained from these soils (see figure 19) show that net arginine ammonification was negatively correlated with soil pH (similar to mineralisation of native organic nitrogen) and *net* arginine nitrification positively with soil pH (dissimilar to nitrification of native organic nitrogen). Arginine nitrification occurred at all soil pH values, it was negligible at pH 3.7 and increased with increasing pH. The investigators conclude that the reason of the larger nitrate concentrations at the lowest pHs in the control soil was due to nitrification occurring in soils with pHs as low as 3.7, while crop growth was negligible under these conditions so that nitrate could accumulate and to increasing plant uptake of nitrate as yield increased with increasing pH so that soil nitrate could decline. Finally, the net total inorganic nitrogen concentrations were larger in soils of low pH than in soils of high pH, and were decreasing with increasing pH. Possible explanations are immobilisation of nitrogen during microbial growth, denitrification or volatilisation of ammonium in soils of high pHs.

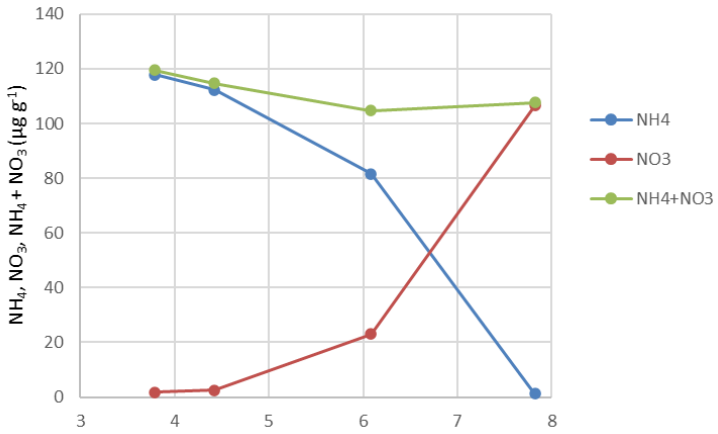

Figure 19 *Net concentration ammonium, nitrate and ammonium plus nitrate (µg g^{-1}) as function of pH. Data obtained from Aciego Pietri and Brookes (2008b).*

In addition to the results (mentioned in paragraph 2.4.2, figure 8) of the study of Kemmitt et al. (2006), it can be mentioned that the investigators observed a positive correlation between nitrification and pH (figure 20a) where nitrification was simulated with the conversion of arginine-N. In contrast, no correlation was present between respiration of arginine-C and pH (figure 20b). Kemmitt et al. (2006) suggest that (when there is a the strong decrease in nitrification with decreasing pH the rate of nitrogen mineralisation may not only be limited by a limitation in the size of the microbial biomass but also by the rate of substrate availability. Nitrogen mineralisation results suggest that pH also caused a shift in the soil microbial community, like the inhibition of nitrifiers at increasing acidity. Increasing acidity results also in an increasing aluminium concentration in the soil solution, which in turn reduces substrate availability and induces toxicity. All these factors reduce the intrinsic activity of the microbial community and so the rate of nitrogen cycling in the soil.

According to Kooijman et al. (2009) the low rate of decomposition in acid or sandy soils or by contrast the high rate in alkaline or loamy soils does not necessarily mean that the net nitrogen mineralisation is low and high respectively. From their study they conclude that in fungi-dominated soil, the net nitrogen mineralisation may be relatively high because low biological activity and gross nitrogen release are compensated for by low microbial nitrogen requirements. In contrast, in a soil dominated by bacteria and earthworms, biological activity may be high but high gross nitrogen release may be counteracted by high microbial nitrogen demand. So, fungal and earthworm-bacteria pathways may fundamentally differ in decomposition and nitrogen cycling. This is another factor to keep in mind when dealing with pH effects on nitrogen mineralisation making it more difficult to do strict statements about pH effects and subsequently to model these effects. Kooijman et al. (2009) noticed differences in the organic layer of fungi versus earthworm and bacteria dominated soil. Fungi dominated soil may show high nitrogen mineralisation due to the higher nitrogen content of the organic matter and the higher fungal C/N in comparison to bacteria dominated soils, and a lower litter consumption (or intake) by soil fauna.

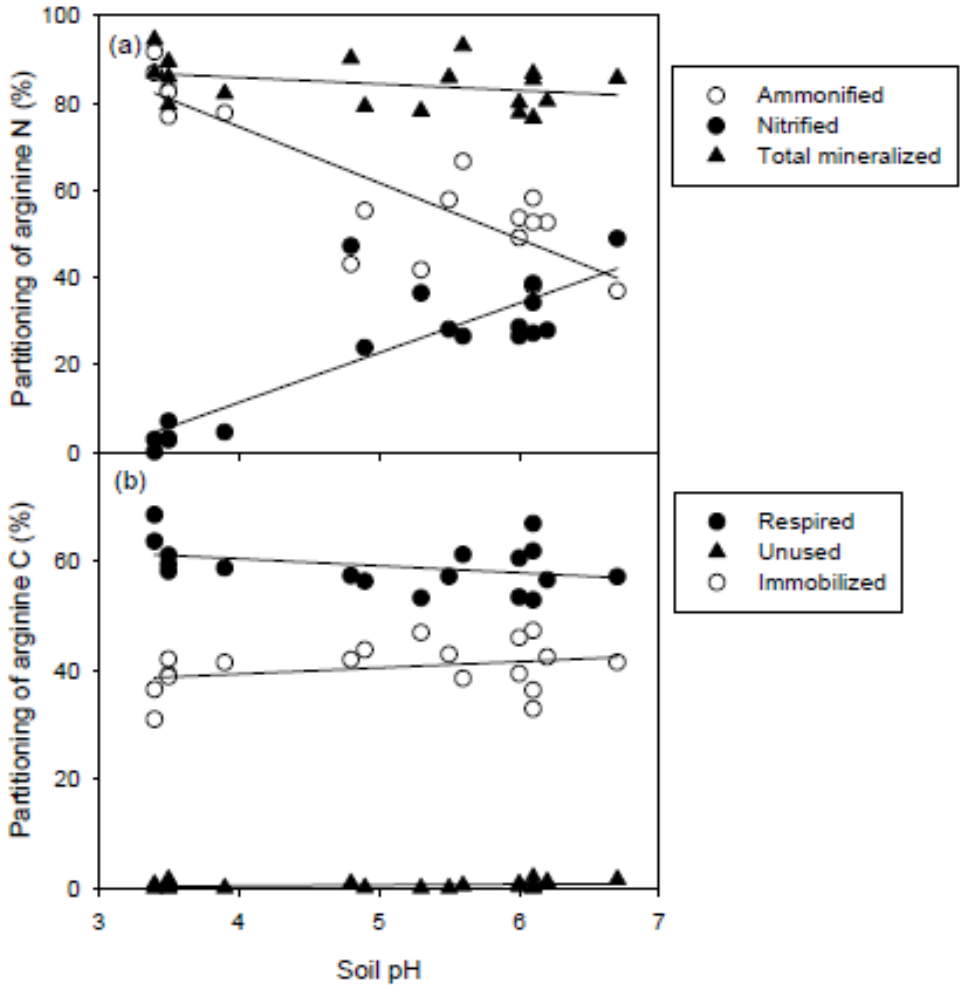

Figure 20 *Effect of soil pH on the fate of (a) arginine-N and (b) arginine-C at the end of the 400h incubation period end (% of the initial amount). (Data points represent individual soil cores.) From: Kemmitt et al. (2006).*

Li et al. (2007) also studied the effect of pH on the mineralisation of native organic nitrogen in naturally salt-affected soils. In their study nitrogen mineralisation of organic nitrogen was highly correlated to soil pH: mineralisation increased linearly with an increase in pH from 5.9 - 10.0 (figure 21). The pH stimulated mineralisation of organic matter was responsible for a deceased amount of organic matter in alkaline salt-affected sandy soils. (Though salinity had an adverse effect on microbial biomass and activity, statistical analysis indicated that salinity was not a significant variable and thus implied that salinity was not a major factor influencing microbial community and activity.)

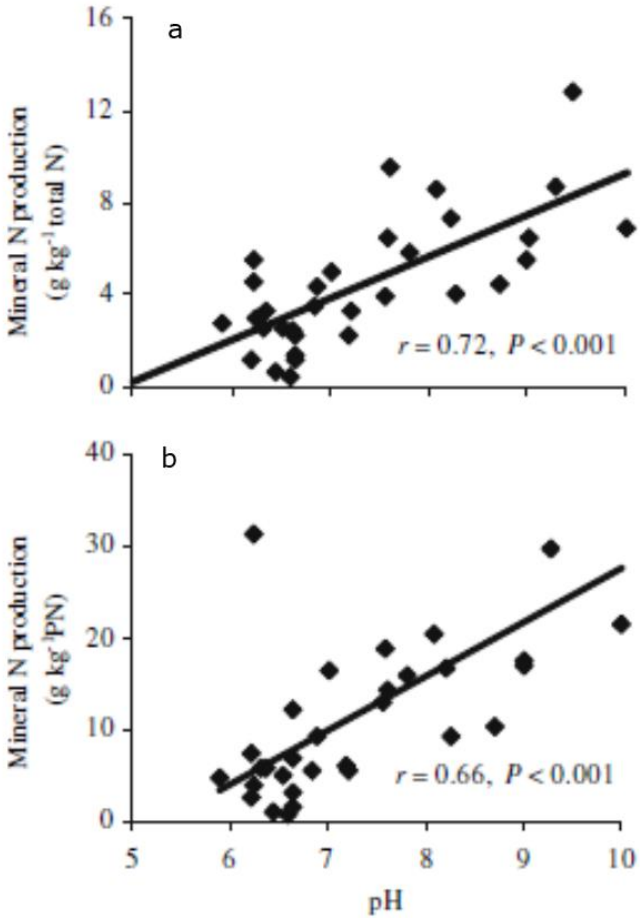

Figure 21 *Mineral nitrogen production expressed as g nitrogen production per kg total organic nitrogen (a) or per kg particulate organic nitrogen (b) over 10-day incubation. From: Li et al. (2007).*

Ouyang et al. (2008) (see paragraph 2.2.8), also revealed a pH influence on the production of ammonium, nitrate and available nitrogen (sum of ammonium and nitrate). Ammonium, nitrate and available nitrogen increases, decreases and decreases resp. with a decrease in pH. The results are graphically presented in figure 22. They suggest that the decrease of organic nitrogen quality, associated with the pH decline (caused by (simulated) acid rain), directly influenced the organic nitrogen mineralisation. Acid rain deposition reduced the production of nitrate. This might be due to a reduced supply of ammonium or to a growth inhibition of nitrifying bacteria. The first cause did not hold actually as ammonium slightly increases with declining pH. The second cause seemed plausible. As nitrification slowed down when soil pH < 6, ammonium became the major nitrogen form in available nitrogen after soil acidification, indicating that nitrification was inhibited by acidification.

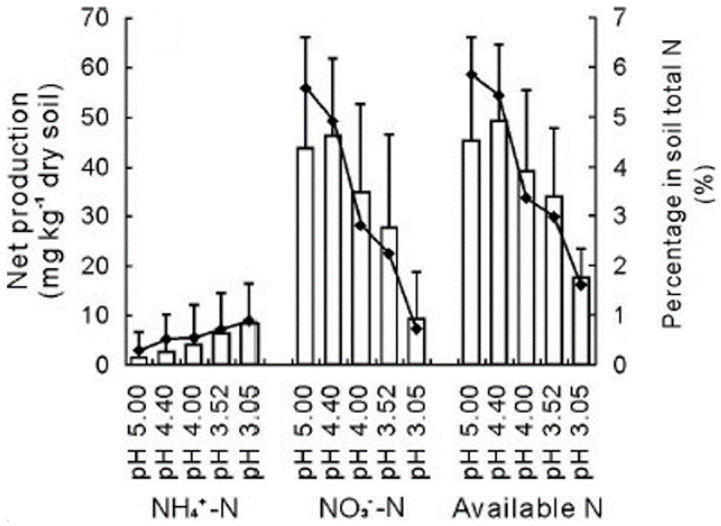

Figure 22 *Effects of different pH (compared to the control with pH 5) on net productions of ammonium, nitrate and available nitrogen (mg kg^{-1} dry soil), and their percentages in soil total nitrogen (the continuous line connected with the dots). Data show mean +/- standard deviation. From: Ouyang et al. (2008).*

Booth et al. (2005) studied nitrogen cycling in ecosystems, including both agricultural, grassland and woodland ecosystems. The additional value of this study in comparison to the preceding ones, is that it includes different types of ecosystems. Ecosystem-wide there is a slightly negative relationship between nitrification and pH (figure 23). Though lower limits of decline in nitrification are given of approximately pH 4.5 (see before), it is noticeable that nitrification goes down to pH 3.0. According to the investigators this was probably due to high production of ammonium in soils of high organic matter content (that tend to have a lower pH) appearing to be the dominant influence on nitrification, despite the decline in pH that often accompanies increasing soil organic carbon. As autotrophic nitrifiers are likely the main nitrifiers (De Boer and Kowalchuk, 2001), the possibility of heterotrophic nitrification accounting for an increased proportion of nitrification at low pH, does not seem the main explanation. However, this does not imply the application of nitrification models for other soil systems to acid ones: the relationships between pH, nitrogen input and nitrifying activity need to be modified for acid soils according to the current knowledge. Apparently, in this case pH cannot be seen independently from other soil factors.

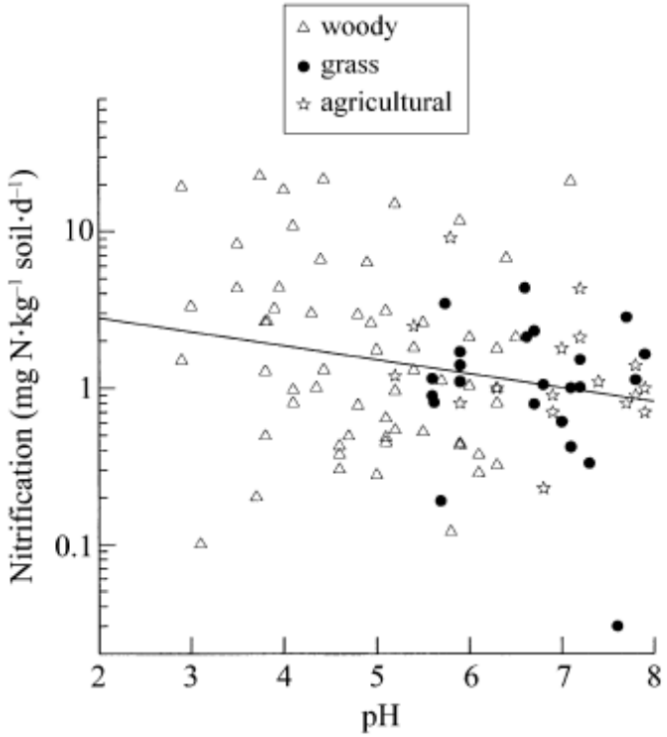

Figure 23 *Relationship of nitrification (mg N^{-1} kg^{-1} d^{-1}) to pH in mineral and organic soil layers from agricultural, grassland, and woodland ecosystems. From: Booth et al. (2005).*

Though the figure of Booth (figure 23) does not give rise to suppose a differentiated relationship for different ecosystems, the study of Cheng et al. (2013) in forest and grassland soils in Alberta (Canada) does: nitrification rates in grassland are six to seven times higher than those in forest (figure 24). Furthermore, this study underpins that also other factors than pH itself affect the pH - nitrification relationship.

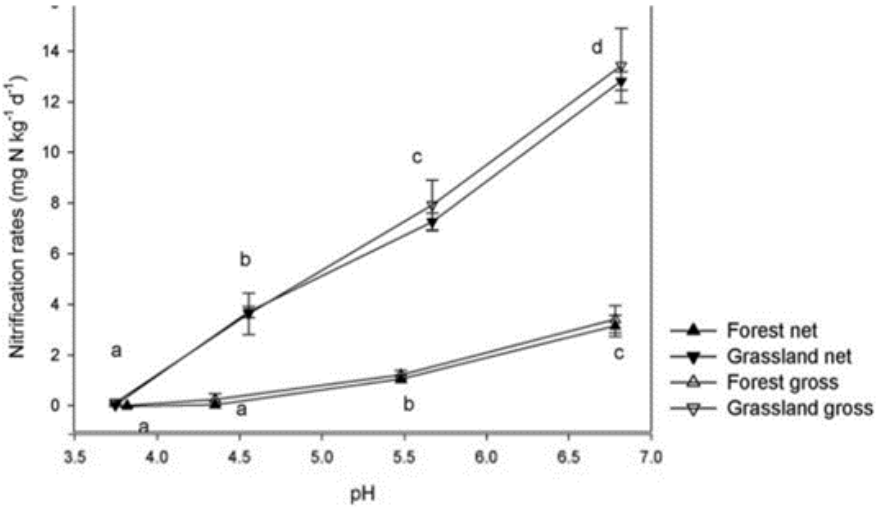

Figure 24 *Soil pH effect on nitrification (mg N^{-1} kg^{-1} d^{-1}) in adjacent forest and grassland soils. Different letters indicate significant differences among pH treatments at $p < 0.001$ for each soil type. Vertical bars are standard deviations (n=3). From: Cheng et al. (2013).*

4 Impacts of pH on carbon and nitrogen mineralisation and nitrification: quantification of relationships

4.1 Quantification of pH - carbon mineralisation relationship

As most studies from paragraph 2.4.2 give cause for to presume a linear relationship between carbon mineralisation and pH, the approach to quantify this relationship is quite straightforward. In our opinion this can be done quite safely when soil pH is between approximately 4.5 and 8. This pH range will generally fulfil as the pH of most (semi)natural areas occurs in this pH range (Wamelink et al., 2011). However, a lower pH in the topsoil (0-10cm) has been observed in some forest soils: 3.7 - 4.0 measured as pH-H_2O and 2.9 - 3.3 measured as pH-KCl (De Vries and Leeters, 2001); this observation demonstrates that a pH-mineralisation relationship at pH < 4.5 is a necessary addition. Especially a pH 4.5 as a lower boundary gets quite some attention in literature. Aciego Pietri and Brookes (2008a) as well Rousk et al. (2009) give rise to think that a pH of 4.5 could be a threshold pH, below which the linear relationship no longer holds. The same holds for a pH of 8 as an upper boundary, as Aciego Pietri and Brookes (2008a) suggest. Thus, our suggestion would be to use a linear pH dependent function like figure 6, 7, 9, 10 and 11 as a good starting point to obtain satisfactorily quantitative estimates of the pH effect on respiration. The pH dependent respiration relationship of figure 10 forms the reference relationship. The relationship for pH < 4.5 will be taken from Rousk et al. (2009) as they only came with observed values in in this pH range.

To be able to mutually compare data from figure 10 with those of figure 6, 7, 9 and 11, we transferred the data as follows:

- the data on the y-as of figure 6 from µmol CO_2 m^{-2} s^{-1} to µg CO_2 h^{-1} g^{-1}, by multiplication with 4.95 (= 44 g CO_2 mol^{-1} 0.030 m^2 (soil) 3600 s h^{-1} / 974.9 g (soil);
- the data on the y-as of figure 7 from µg CO_2 h^{-1} g^{-1} (SOC) to µg CO_2 h^{-1} g^{-1}, by multiplication with g SOC g^{-1} soil;
- the data on the y-as of figure 9 from mg CO_2 $kg^{-1}h^{-1}$ to µg CO_2 h^{-1} g^{-1}, by multiplication with (1000 µg CO_2 (mg CO_2)$^{-1}$) * (10^{-3} kg soil * g^{-1} soil),
- the data on the y-as of figure 11 from µg CO_2 h^{-1} g^{-1} (SOC) to µg CO_2 h^{-1} g^{-1}, by multiplication with g SOC g^{-1} soil.

The drawn regression lines in the figures 6, 7, 9, 10 and 11 are:

- R1 (fig 6) = 4.08 x pH -11.51, and 5.0 < pH < 6.0
- R2 (fig 7) = 0.126 x pH – 0.602, and 6.0 < pH < 10.0
- R3 (fig 9) = 0.21 × pH – 0.23, and 4.0 < pH < 8.0 (soil depth 0 – 10 cm) and
- R3 (fig 9) = 0.14 x pH – 0.42, and 4.0 < pH < 8.0 (soil depth 10 – 20 cm)
- R4 (fig 10) = 0.055 × pH + 0.071, and 4.5 < pH < 8.3 and
- R4 (fig 10) = 0.44 × pH - 1.66, and 4.0 < pH < 4.5
- R5 (fig 11) = 0.61 × pH + 0.22, and 4.0 < pH < 8.0

with R: respiration in µg CO_2 h^{-1} g^{-1}.

These regression lines, provided with the equations, are depicted in figure 25.

The regression results above show that the pH dependency deviate considerably: the slope can deviate a factor 10 (figure 10 versus figure 7, 9 and 11, with 4.5 < pH < 8.3), or even a factor 100 (figure 7 versus figure 6, with 4.5 < pH < 8.3). Thus we conclude that other environmental factors such as soil type and soil temperature as well as spatial (or temporal) field variation in respiration itself might explain the large differences in the regression results above. This conclusion might plead for a comprehensive meta-analyses on the pH – respiration relationship. It is, however, questionable if a meta-analysis will significantly summarise the pH-dependent respiration relationship: there will likely be too many different factors between

the different studies as well as many interactive effects in individual studies that could not be accounted for in a meta-analysis. In addition, sufficient data for the relevant factors are not always mentioned in the publications. Hence, it is questionable if a relationship developed from a separate study (like the influence of soil moisture on pH-respiration relationship) will be (highly) comparable with another study.

Figure 25 clearly shows that all relationships show a positively linear relation of respiration with pH. A weak relationship may point to a certain level of functional redundancy (see also section 3.1.1). A first, cautious step in modelling might be to take 1) a kind of average relationship, 2) to choose a relationship from figure 26 that corresponds with own field respiration measurements to determine its order of magnitude. Next, if you in line with SMART2, wants to use a reduction function you next need to mathematically transform this function into a reduction function.

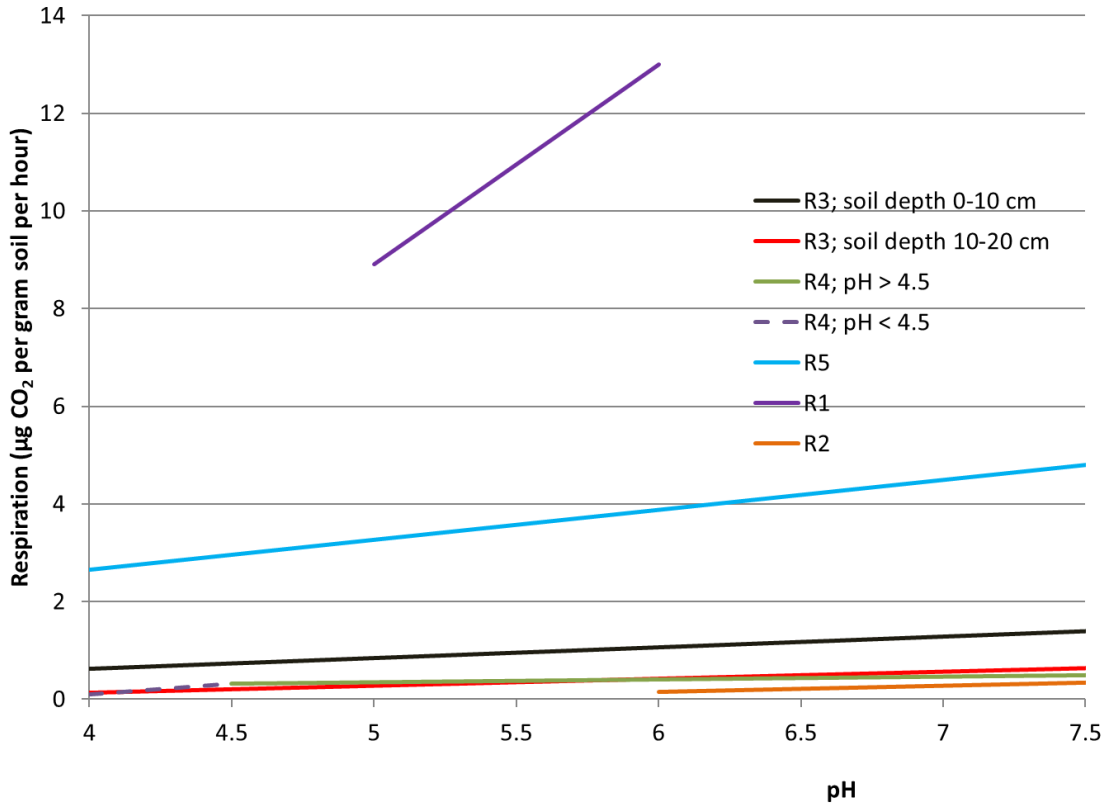

Figure 25 *Regression lines and accompanying equations, depicting respiration (µg CO_2 g^{-1}soil h^{-1}) as function of pH (for legend see text).*

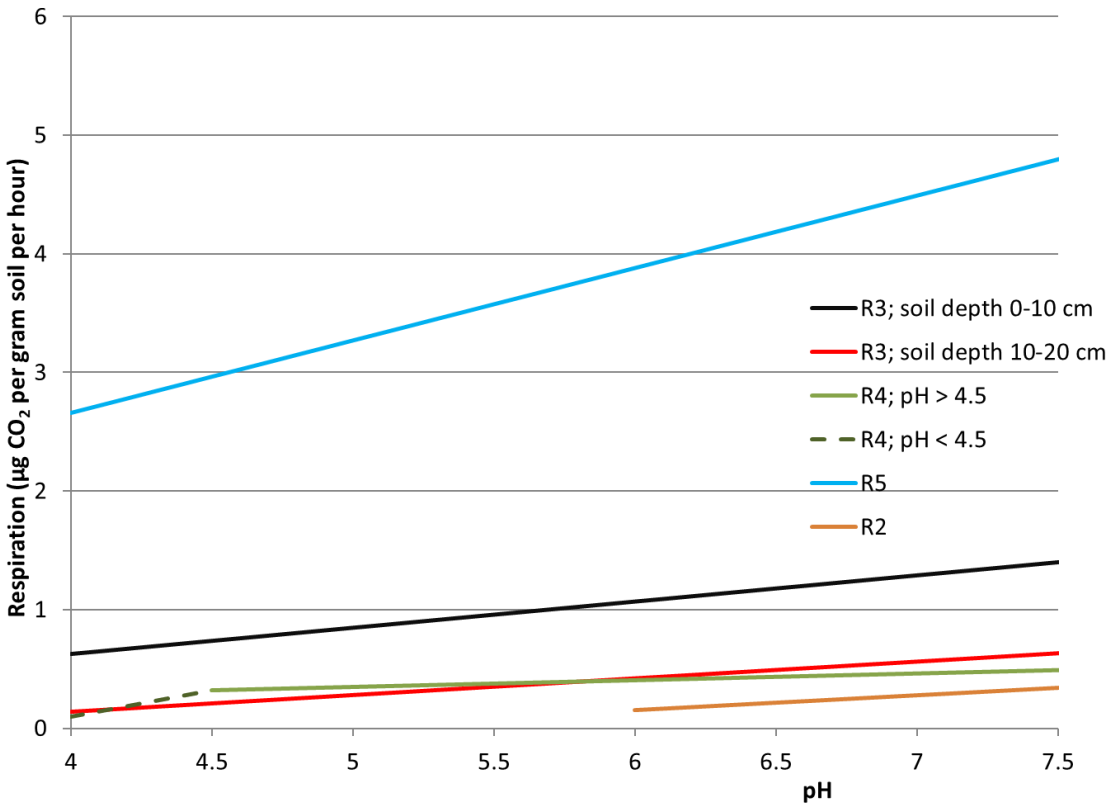

Figure 26 *A duplicate of figure 25, with R1 excluded to improve picture's quality (for legend see text).*

Nevertheless, the studies of Hobbie and Gough (2004) and of Ouyang et al. (2008) show that besides pH, nutrient availability (in particular nitrogen) is also is an important factor in the decomposition of organic matter. Analogously, Blagodatskaya and Anderson (1998) pointed to substrate as an important factor in decomposition and discovered a pH - substrate interaction effect, making our ideas on the pH effects on decomposition even more complicated. In this case the pH relationship will depend on the nutrient availability or substrate quality, complicating the modelling of carbon mineralisation. Thus, it is highly recommended not to trust blindly on the supposed linear relationships of figure 25. If models used in research projects require accurate respiration estimates, then a field trial is highly recommended. If however, a quick rough estimate fulfils, the first or second step of the last paragraph is recommended.

4.2 Quantification of pH - nitrogen mineralisation / nitrification relationship

In view of nitrogen mineralisation the approach seems different and is more complicated too. First of all we have the existence of two processes: ammonification and nitrification (in a broad sense). As written in paragraph 2.5.2, pH - ammonification c.q. nitrification relationships basically both have an optimum curve (Wood (1988) and Paul and Clark (1989); Olness (1999) also mentioned an optimum curve for nitrification) but we descry difference in pH optimum for ammonification and nitrification (6 – 8, 7.5 – 8 resp.) and in pH sensitivity between ammonification and nitrification (nitrification is much more pH sensitive) and variation in the pH-minimum below which nitrification is severely limited (4 – 5.5). This variation of 1.5 pH units shows that other factors might intervene with the nitrification, making pH modelling dependent from other factors as well. As nitrification normally increases with higher pHs, it culminates into lower ammonium concentrations at higher pHs. The increase of pH does not necessarily mean a higher nitrogen mineralisation because of - due to an increased microbial activity - enlarged immobilisation (Williams, 1972; Kooijman et al., 2009). In contrast to nitrogen, immobilisation of CO_2 does not play a role in the carbon balance of microorganisms like ammonium does in the nitrogen balance.

Despite the mentioned optimum relationship of the ammonification, the ammonium concentrations can still be high at a low soil pH. Other factors appear to intervene or even overrule the pH effect and so pH is not all-determining in explaining nitrification. Falkengren-Grerup et al. (1998) points to nitrogen deposition improving the quantity of nitrogen and the quality and so the decomposability of organic matter at low pHs (see paragraph 2.6.3); due to significant nitrogen deposition the pH minimum of 5.4 of nitrification lowered to around 3.5. In addition, we have to be aware that the ammonium concentration is the result of the production of ammonium by ammonification and the consumption of ammonium by nitrification as well as the uptake by plants, autotrophs and heterotrophs (immobilisation) as mentioned by Tate (2000), Booth et al. (2005), Robertson and Groffman (2007) and Kooijman et al. (2009).

Like the ammonium concentrations, also the nitrate concentrations do not show a pH optimum dependency (except one research result from Falkengren-Grerup et al. (1998): figure 17 bottom left). This optimum exists around pH 4, much lower than the optimum of 7.5 – 8 mentioned by Wood (1988) and Paul and Clark (1989). A long right-skewed tail of this optimum gives a nearly (overall) negative relationship of nitrification with pH. This negative relationship was motivated by adaptation of nitrifiers to a low pH (time dependent) and by a sufficient supply of ammonium by ammonification at low pHs. The first point does take time because the soil system has to obtain a new equilibrium and this cannot currently be modelled by SMART2. The second point stresses the availability of ammonium for the process of nitrification as an important factor (see also paragraph 2.5.2) and mentioned by Booth et al. (2005) as being more important than pH (nitrification can increase with descending pH if ammonification is sufficient). At a low pH a relatively large amount of SOM and ammonium is available for nitrification (Booth et al., 2005). Aciego Pietri and Brookes (2008a) discovered the pH dependent uptake of nitrate by plant roots as a factor interfering with the pH dependent production of nitrate by nitrification (of native organic matter), responsible for the ultimate nitrate concentration of the soil. As plant growth declines with decreasing pH the uptake of nitrate decreases and the soil nitrate concentration could increase. In this sense, the nitrate uptake interferes the nitrate (from nitrification) - pH relationship. Foereid et al. (2006) noticeably remarks that as liming usually increases plant productivity partly through increased nitrogen mineralisation, the net effect of an increase in pH on ecosystem storage is difficult to predict *without* experimentation.

The negative relationship just mentioned contradicts the positive relationship mentioned by Olness (1999), Kemmitt et al. (2006), Li et al. (2007) and Aciego Pietri and Brookes (2008a). Kemmitt et al. (2006) and Aciego Pietri and Brookes (2008a) used in this context arginine as organic nitrogen source. Kemmitt et al. (2006) also mentioned the ammonium availability, like Booth et al. (2005) did, that increasingly is reduced by aluminium at decreasing pH. In addition, they talked about inhibition of the nitrifiers by acidity and toxicity at low pH. Olness (1999) added to the inhibition of nitrifiers, the decline of the quality of organic matter as a factor responsible for a decrease of nitrification with decreasing pH.

All in all we may conclude that 1) modelling of ammonification and nitrification relationships to pH is not straightforward: the relationships deviate between the literature sources c.q. soil systems and even opposites are found (as is the case with nitrification), 2) the availability of ammonium might be more important than the pH in case of nitrification. Actually this remark can be generalised: to model the pH dependency of ammonification and nitrification accurately it is indispensable to know what the consumption of ammonium and nitrate in soil systems are as well as their pH dependencies. To summarise; it is quite difficult to give a generally applicable and accurate pH dependent production function of ammonium and nitrate by ammonification and nitrification. In fact, in our opinion such functions have to be developed in close cooperation with knowledge from the concerning soil system itself (which processes interfere with ammonium and nitrate).

To be able to mutually compare data the units on the y-axis form the figures 17, 19-22 have been converted to µg N g^{-1}(soil) d^{-1} we transferred the data as follows:

- the data on the y-as of figure 17 from µg N g^{-1} LOI d^{-1} to µg N g^{-1} soil d^{-1}, by multiplication with 0.0099 g organic matter g^{-1} soil (0.0099 the organic matter content of the soil);
- the data on the y-as of figure 17 from µg N g^{-1} soil to µg N g^{-1} soil d^{-1}, by multiplication with 1/50 d^{-1} (incubation period 50d);
- the data on the y-as of figure 20 from % to µg N g^{-1} soil d^{-1}, by multiplication the percentage with 140 mg N kg^{-1} soil × 24h d^{-1} × 1/408 h^{-1} (the initial amount of arginine was 140 mg per kg soil and the incubation period was 408 h) (mg N kg^{-1} soil is mathematically equivalent to µg N g^{-1} soil);
- the data on the y-as of figure 21 from g N kg^{-1} (total N) to µg N g^{-1} soil d^{-1}, by multiplication with 10^6 µg Ng^{-1} N × 0.42 g N kg^{-1} soil × 10^{-3} kg soil g^{-1} soil;
- the data on the y-as of figure 22 from mg N kg^{-1} soil to µg N g^{-1} soil d^{-1}, by multiplication with 1/65 d^{-1} (incubation period 65d) (mg N kg^{-1} soil is mathematically equivalent to µg N g^{-1} soil).

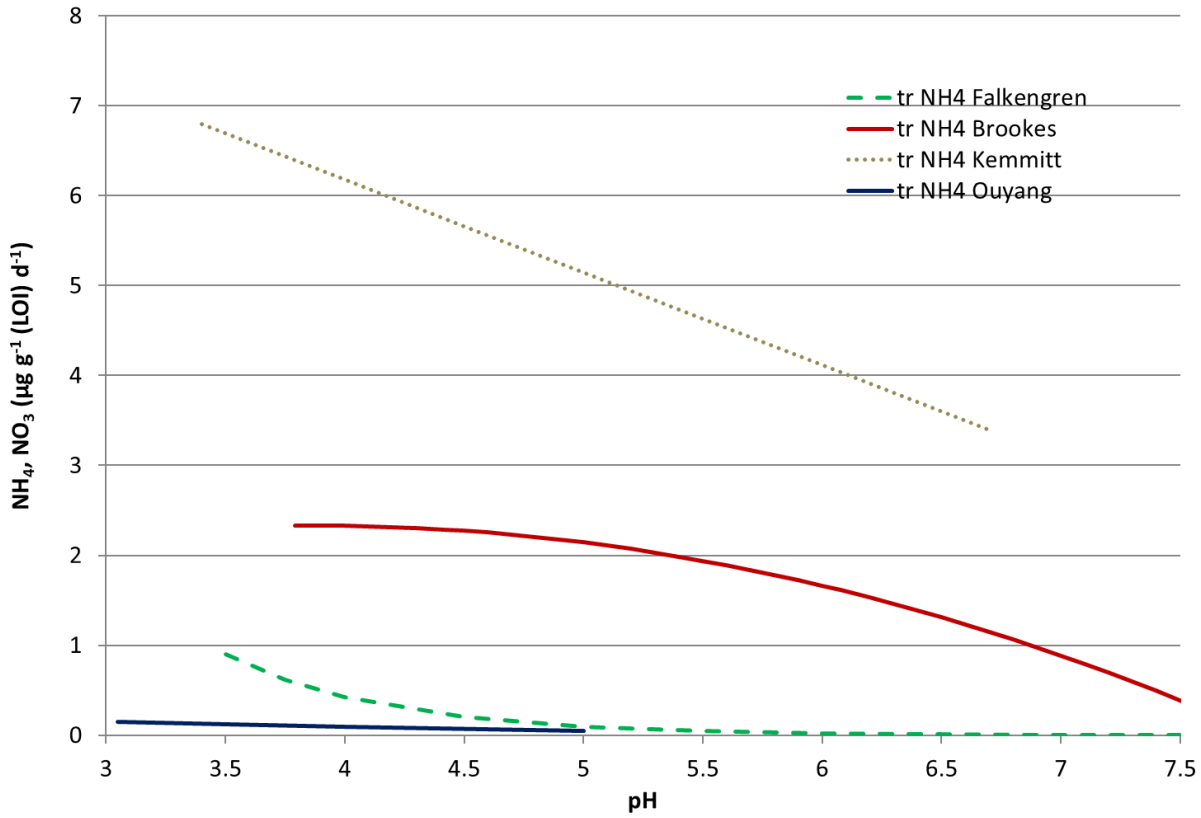

Figure 27 *Net NH_4 production (µg g^{-1} LOC d^{-1}) as function of pH (pH-KCl).*

The accompanying mathematical expressions are:

- tr NH4 Falkengren = $9\exp(pH-3.5)^2$ and 3.5 < pH < 7.5;
- tr NH4 Brookes = $-0.15pH^2 + 1.14pH + 0.12$ and 3.8 < pH < 7.8;
- tr NH4 Kemmitt = $-1.03pH+10.3$ and 3.4 < pH < 6.7;
- tr NH4 Ouyang = $-0.05pH + 0.30$ and 3.1 < pH < 5.0;

with: tr NH4: NH_4^+ production in µg NH_4^+ g^{-1} soil d^{-1}.

Figure 27 shows the general picture of the decline of ammonification with pH. In addition, it shows the variability in the pH dependency of ammonification. To give an suggestion to start with in SMART2, one might choose one the relationships of figure 27 at which the soil system of own study resembles the most at the system that was studied in literature. Another suggestion might be to determine some sort of average relationship out of the relationships depicted in figure 27.

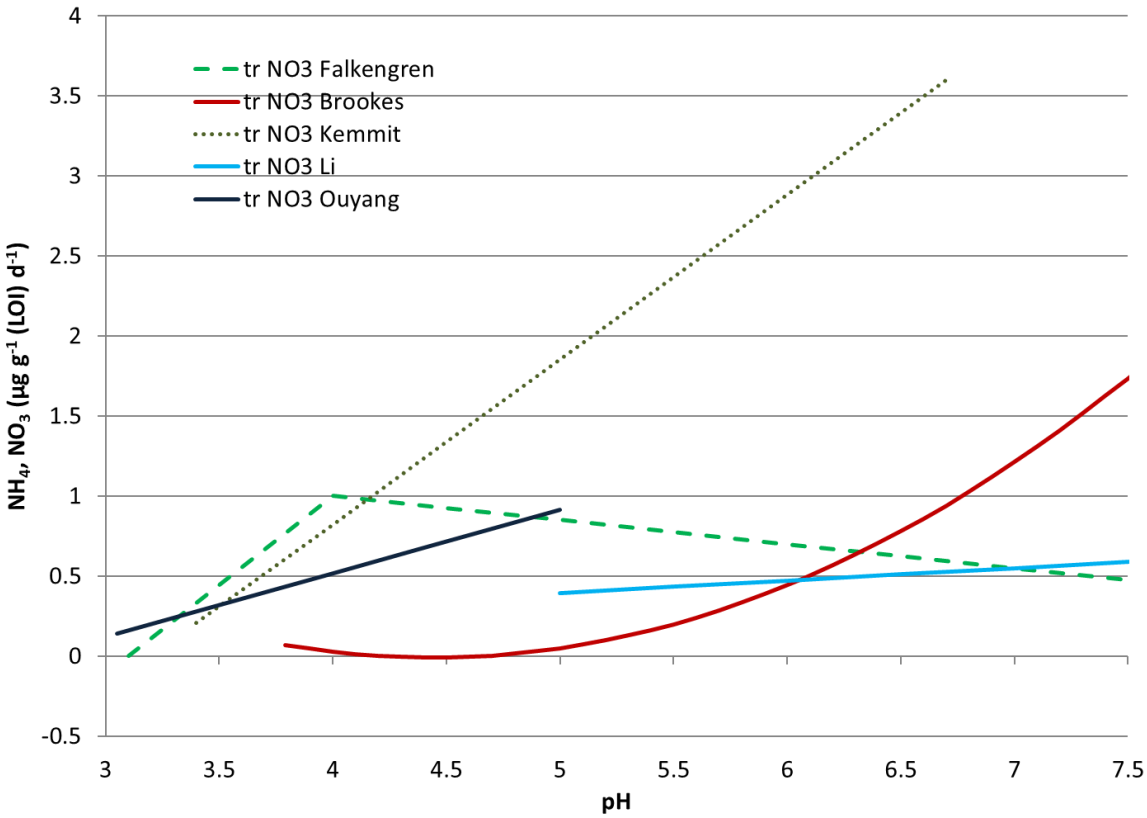

Figure 28 *NO_3 production (µg g^{-1} LOC d^{-1}) as function of pH (pH-KCl).*

- tr NO3 Falkengren = 11.11pH - 34.44 and 3.1 < pH < 4.0;
- tr NO3 Falkengren = -1.5pH + 16 and 4.0 < pH < 7.5,
- tr NO3 Brookes = $0.187pH^2$ -1.660pH + 3.68 and 3.79 < pH < 7.82;
- tr NO3 Kemmitt = 1.029pH - 3.29 and 3.4 < pH < 6.7;
- tr NO3 Li = 0.0785pH and 5.0 < pH < 10.0
- tr NO3 Ouyang = 0.397pH – 1.07 and 3.05 < pH < 5.0;

with: tr NO3: NO_3^- production in µg NO_3^- g^{-1} soil d^{-1}.

Figure 28 shows the general picture of the increase of nitrification with pH and the variability in the pH dependency of ammonification. In case of nitrification the same suggestions are recommended as those given for ammonification.

When the pH relationships of ammonification (figure 27) and nitrification (figure 28) are compared to the pH relationships of respiration (figures 25), it can be concluded that ammonification and nitrification generally are much more pH dependent/sensitive than carbon mineralisation.

5 Conclusions and recommendations

In the chapter the we recapitalised the major conclusions and recommendations of this study.

5.1 Conclusions

It is important to consider that the pH influence on soil microbiology cannot be seen independently of the pH influence on plant growth and rhizosphere ecology as they influence the supply and quality of organic matter, i.e. the source of the material to be decomposed. This organic matter stems from both litter and roots. Notably, roots are the most important carbon source (Rasse et al., 2005).

Soil pH is a master variable in soil microbial processes, with effects on organic matter decomposition, nutrient cycling and nitrogen transformation. It is a powerful factor in influencing the size, activity and community structure of the soil microbial community responsible for the decomposition. In addition, substrate competition between different community members can explain differences in soil pH effects on decomposition and nitrogen transformation. Furthermore, soil pH can both reduce the microbial biomass and activity as well the input of organic matter to the soil (Li et al., 2020).

Changes in soil pH within a single soil type can have marked effects on soil microbial biomass and microbial activity, most likely due to an increase of extractable aluminium as soil pH decreases. This clearly illustrate the indirect effect of pH on microorganisms, but there also direct effects were observed. A direct effect of pH on enzyme and metabolic activities of the corresponding microorganisms (direct effect of pH on microorganisms) has been observed as well as an indirect effect of pH on decomposer community. The pH dependencies of decomposition reaction rates has been ascribed to combined effects on toxic effects of aluminium, enzyme activities, and decomposer community. This is a clear demonstration of the direct as well indirect effects of pH on microorganisms, effects we have to be aware of, as was demonstrated by figure 2.

For many processes, the overlapping abilities of microorganisms to mineralise organic matter provide a functional redundancy that allows terrestrial ecosystems to function over a broad pH range. However, for certain processes like ammonification and nitrification, that are carried out by only a few species of microorganisms, the impact of pH is much greater, and significant changes in nitrogen transformation rates are observed over relatively small pH increments. So, respiration is less pH sensitive than ammonification and nitrification are. This argues for the use of a distinct mathematic relationships (or reduction functions) for the pH dependent modelling of respiration (carbon dioxide production), ammonification (ammonium production) and nitrification (nitrate production).

Figure 2 shows that pH has many influences on soil processes with mutual dependencies besides the process-specific pH response functions. This makes modelling of pH decomposition relationships not straightforward and also soil system dependent, though the soil dependency can be accounted for. Hence, it is highly questionable if a generally applicable relationship will fulfil for accurate modelling of carbon dioxide, ammonium or nitrate production. In our opinion relationships have to be determined for each separate soil system ("with its own figure 2"). The determination of such relationships is not so easy/straightforward. Despite, a choice out of the presented relationships in the figures 25, 27 and 28 can be made or a kind of average relationship can be calculated that might provide rough production rates that can function as a first order approach in modelling the pH influences on decomposition rates.

5.2 Recommendations

As clay influences the stabilisation of SOM and this stabilisation is dependent on pH, it serves recommendation to take the clay content as a pH dependent factor into consideration. Therefore, in view of modelling purposes one must not solely focus on pH as a separate factor on the specific decomposition process involved, but also consider other decomposition relevant factors if they are pH dependent. This study also has shown that other factors like nitrogen deposition (which is absent in figure 2, unlike clay content or CEC) even can overrule the pH effect, underpinning even more a system-based approach. In this case an independent use of process-specific pH response functions (as is the case in mutual dependencies) will not fulfil. Another system relevant factor is plant nutrient uptake or plant productivity. As plant productivity interferes with nitrogen mineralisation in view of pH, the net effect of an increase in pH on ecosystem storage is difficult to predict without doing experiments.

As nitrification (both autotrophic and heterotrophic) can be performed by a lot of different microorganisms with specific behaviour like pH adaptation or specific processes like the comammox process, it serves recommendation to determine the microbial composition belonging to nitrification to understand and next to explain/quantify the pH dependent nitrification of a certain soil. Furthermore, it serves also recommendation to be aware of or to follow other processes like denitrification as they can co-declare the fate of organic nitrogen.

As pH – respiration/mineralisation relationships also depend on environmental factors like soil type and temperature, we duly recommend to consider these factors in the study of these relationships. If these relationships also influenced by spatio-temporal variability (such as the spatio-temporal variability in pH) as well as other confounding factors, it might be even better to replace a meta-analysis with a well-designed experimental field study. As long-term field experiments (e.g. pH adaptation by liming) can show different results than short-term ones, it is important to take the time span of experiments into consideration. Finally, one must be careful to generalise experimental results to common rules as contrasting results can occur, indicating that other factors may be involved in the processes of respiration and nitrogen mineralisation.

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Report 3342
ISSN 1566-7197

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