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Evolution of soil solution chemistry in temperate forests under
decreasing atmospheric deposition in Flanders

Thesis submitted in fulfillment of the requirements
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Forest and Nature Management

Illustrations on the cover:

Front: ICP Forests Level II plot in a European beech (*Fagus sylvatica* L.) stand in the forest of Wijnendale (July 2016) (photo: Arne Verstraeten)

Back: Suction cup lysimeters for soil solution sampling in the Level II plot in a Scots pine (*Pinus sylvestris* L.) stand in 'De Inslag' in Brasschaat (August 2016) (photo: Yvan De Bodt)

Woord vooraf

Bossen vormen in Vlaanderen op veel plaatsen de natuurlijke climaxvegetatie en door hun complexe structuur herbergen ze zowel naar soortenrijkdom als functionaliteit wellicht de hoogste diversiteit onder de terrestrische ecosystemen. Ze beschermen ons drinkwater, vormen een buffer tegen bodemerosie, slaan koolstof op, voorzien ons van hout en fungeren als groene longen, door zuurstof vrij te geven en polluenten uit de lucht te filteren, om maar enkele van de vele ecosysteemdiensten te noemen die het bos vervult. Precies omwille van die weldadigheid van het bos voor mens en milieu nemen bosonderzoekers en -beheerders multifunctionaliteit als een onmisbaar deelaspect mee in de besluitvorming, en dit al decennia lang vóórdat het begrip "ecosystem services" een modewoord werd.

Toch heeft de mensheid doorheen de geschiedenis, waarin bossen steeds een haast onmisbare rol vervulden, het bos veel meer gebruikt en vernield dan respect betoond en gekoesterd. Ondanks een toenemend natuur- en milieubewustzijn blijkt dit in Vlaanderen ook nu nog symptomatisch uit de vaak weinig zorgzame manier waarop met ons natuurlijk patrimonium wordt omgegaan: te veel ecologisch waardevolle oude bomen worden gekapt, dik dood hout in parken wordt in opkuiswoede weggehaald en bosranden worden alom volgestort met afval. Bossen genieten ook nog steeds onvoldoende wettelijke bescherming en bij de herbestemming van gronden krijgt bebossing nauwelijks kansen waardoor Vlaanderen nog steeds wacht op de 10000 ha bosuitbreiding die 20 jaar geleden werd beloofd. Dat we leven in één van de weinige regio's in Europa waar de schaarse bosoppervlakte niet eens exact gekend is en de jongste decennia vrijwel stabiel bleef is dus misschien niet zo verwonderlijk.

Deze thesis bundelt een aantal resultaten gebaseerd op 30 jaar langetermijnonderzoek naar de effecten van luchtverontreiniging in Vlaamse bossen. Deze monitoring is uniek omwille van de lange looptijd en de wetenschappelijk waardevolle data die ze genereert, gesteund op geharmoniseerde methodieken voor staalname, laboanalyse, datavalidatie en -rapportering, vastgelegd in standaardprotocols die door de internationale Expert Panels van ICP Forests up-to-date worden gehouden. Het project in Vlaanderen vormt op die manier een onderdeel van een pan-Europees netwerk, en draagt bij tot een waaier aan hoogstaand wetenschappelijk onderzoek dat leidt tot belangrijke inzichten inzake ecosysteemprocessen en factoren die de gezondheidstoestand van bossen beïnvloeden. Ik ben dan ook bijzonder trots dat ik de kans heb gekregen om aan dit project mee te

werken, de noodzaak en het belang ervan te verdedigen en de verzamelde gegevens te verwerken en te publiceren. Dat de resultaten van dit werk wijzen op een minder sterk voortschrijdende verzuring en een beperkt herstel van stikstofverzadiging in Vlaamse bossen als gevolg van een dalende luchtvervuiling met zwavel en stikstof is een positief signaal, dat weliswaar contrasteert met de onzekere vooruitzichten omwille van mogelijk toenemende negatieve effecten van de klimaatverandering.

Het spreekt voor zich dat ik bij de presentatie van dit werk aan een groot aantal mensen bijzondere dank en erkentelijkheid verschuldigd ben.

Om te beginnen wil ik Stefaan en Steven hartelijk danken om voor mij te willen optreden als de officiële promotoren van mijn doctoraatsonderzoek, alsook voor hun inhoudelijke bijdrage aan dit werk, en de vele positieve steun en motivatie die ik bij het uitwerken van de laatste twee papers en het uiteindelijke opbouwen van de thesis en voorbereiden van het eindexamen van hen meekreeg.

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De resultaten van dit onderzoek konden ook slechts tot stand komen dankzij de toewijding en permanente inzet van onze gemotiveerde technici tijdens de vele, vaak

routinematige staalnames, die noodgedwongen soms ook bij barre weersomstandigheden moeten worden uitgevoerd. Ik heb vaak zelf ervaren dat dit behoorlijk wat van het menselijk lichaam kan vergen. Ik ben mijn collega's Yvan De Bodt, Luc De Geest, Eddy Smesman, Mathieu Pieters, Koen Willems, Koen Vervaet, Arthur De Haeck, Pieter Dhaluin en Bart Praet dan ook bijzonder erkentelijk voor het feit dat zij steeds het beste van zichzelf hebben gegeven, om een zo hoog mogelijke kwaliteit van de verzamelde data te kunnen garanderen. Hierbij wil ik ook mijn collega Geert Sioen hartelijk danken voor het coördineren van de planning van het veldwerk, waardoor de metingen en staalnames ook ondanks de hoge werkdruk voor de technici steeds vlot konden blijven gebeuren. Bijzondere vermelding en dank verdienen ook Luc Willems, Yves Verhaeghe, Wim Stevens, Koen Maertens, Mark Schuermans en Paul Meulemans, die voor ons al jarenlang vrijwillig de lysimeters in de proefvlakken op onderdruk brengen tijdens de dagen voorafgaand aan de staalname, een hulp die onmisbaar is om op regelmatige basis goede stalen van de bodemoplossing te kunnen nemen.

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Contents

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

ACID	Potentially acidifying compounds
ANC	Acid neutralizing capacity
BD	Deposition in the open field
BS	Base saturation
CEC	Cation exchange capacity
DOM	Dissolved organic matter
EMF	Ectomycorrhizal fungi
FFC	Forest floor carbon
LOESS	locally weighted polynomial regression
LOQ	Limit of quantification
LTER	Long-Term Ecosystem Research
MAP	Mean annual precipitation
MAT	Mean annual temperature
OM	Organic matter
PAS	Programmatic Approach to Nitrogen
SOC	Soil organic carbon (mineral soil)
TF	Stand deposition (sum of throughfall and stemflow deposition)
pH	Potential of hydrogen, -log(H^+ concentration)
SOM	Soil organic matter

Symbols

p	Significance of a statistical test
pK_a	Acid dissociation constant at logarithmic scale
R^2	Coefficient of determination (the proportion of the variation in the dependent variable that is predictable from the independent variable(s))
ρ_S	Spearman's ρ (rho)

Chemical compounds

Al	Aluminium
Al^{3+}	Aluminium(III) ion
Al_{tot}	Total aluminium

BC	Base cations (= $Ca^{2+} + K^+ + Mg^{2+}$)
BC:Al$_{tot}$	The molar ratio of BC and Al$_{tot}$
BC:N	The molar ratio of BC and N
C	Carbon
Ca^{2+}	Calcium ion
Ca:Al$_{tot}$	The molar ratio of Ca^{2+} and Al$_{tot}$
$CaCl_2$	Calcium dichloride
$CaCO_3$	Calcium carbonate
CH_4	Methane
Cl^-	Chloride ion
C:N	The molar ratio of C and N
CO	Carbon monoxide
CO_2	Carbon dioxide
DIN	Dissolved inorganic nitrogen
DOC	Dissolved organic carbon
DOC:DON	The molar ratio of DOC and DON
DOC:NO_3^-	The molar ratio of DOC and NO_3^-
DON	Dissolved organic nitrogen
DON:DIN	The molar ratio of DON and DIN
DON:TDN	The molar ratio of DON and TDN
Fe	Iron
Fe$_{tot}$	Total iron
H	Hydrogen
H^+	Hydrogen ion (proton)
HCO_3^-	Bicarbonate ion
H_2CO_3	Carbonic acid
HNO_2	Nitrous acid (HONO)
HNO_3	Nitric acid
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
K^+	Potassium ion
Mg^{2+}	Magnesium ion
N	Nitrogen
N_2	Nitrogen gas

Na^+	Sodium ion
NH_3	Ammonia
NH_4^+	Ammonium ion
$NH_4^+:NO_3^-$	The molar ratio of NH_4^+ and NO_3^-
NH_y	Reduced nitrogen
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_2^-	Nitrite ion
NO_3^-	Nitrate ion
NO_x	Nitrogen oxides ($NO + NO_2$)
NO_y	NO_x + reservoir species ($NO + NO_2 + N_2O_5 + PAN + HNO_3 + HNO_2 + NO_3$ + organic nitrates + particulate nitrate)
N_2O	Nitrous oxide
N_2O_5	Dinitrogen pentoxide
N:P	The ratio of N and P
O	Oxygen
O_2	Oxygen gas
O_3	Ozone
P	Phosphorus
PAN	Peroxyacetyl nitrates
S	Sulphur
SO_2	Sulphur dioxide
SO_4^{2-}	Sulphate ion
TDN	Total dissolved nitrogen
TKN	Total Kjeldahl nitrogen

1 INTRODUCTION

1.1 Emissions and atmospheric depositions in the anthropocene

1.1.1 Definitions

Since the Earth's earliest atmosphere was formed by the impact of meteorites and volcanic outgassing, its chemical composition continuously changed, driven by variation in geological activity and the emergence and evolution of life, the primary producer of atmospheric oxygen (O_2) (Kasting, 1993; Lyons et al., 2014). Recently, also man began to alter the composition of the atmosphere at a rate unparalleled in the history of the Earth. This new era is called the *anthropocene* (Lewis and Maslin, 2015). Modern human activities like intensive farming practices, burning of fossil fuels and certain industrial processes, discharge quantifiable amounts of chemical substances in the atmosphere, called anthropogenic *emissions* (Granier et al., 2011). These substances consist partly of gasses, which could act as air pollutants, e.g., carbon monoxide (CO), sulphur dioxide (SO_2), reactive nitrogen (N) in oxidized (NO_y) and reduced form (NH_y) and ground level ozone (O_3). Certain emitted gasses, and particularly carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), act as greenhouse gasses and strongly contribute to current global warming (increasing mean temperatures) and other aspects of climate change (Wigley, 1998). Besides gasses, anthropogenic emissions also consist of particulate matter, i.e. suspended microscopic solid or liquid organic and inorganic matter, including soot, smoke, ash and dust (Donahue et al., 2009; Gieré and Querol, 2010).

Anthropogenic emissions increase the air concentrations of pollutants above natural (biogenic) background levels, which may fluctuate depending on temporal variation in volcanic activity, soil emissions, biomass burning, sea spray and lightning (Holland et al., 1999; Simpson et al., 1999; Granier et al., 2011). Air pollutants are subjected to solar radiation and local weather and can be physico-chemically transformed and transported over varying distances through the atmosphere (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000; Zheng et al., 2015). Air pollutants are removed from the atmosphere through various deposition mechanisms and will end up on water, land or vegetation in quantifiable amounts, called *atmospheric depositions*, which could have deleterious impacts on ecosystem functioning (Phoenix et al., 2006; de Vries et al., 2014a; de Vries et al., 2014b).

This thesis focuses on the impact of gaseous emissions and atmospheric depositions on temperate forest ecosystems, particularly S and N compounds. The effects of climate change are also addressed when relevant, but are not the core subject of this work.

1.1.2 Historical background

Human activities (e.g. deforestation) have affected the composition of the atmosphere for several millennia, but pre-industrial emissions had only a small impact on present-day climatic change and levels of atmospheric deposition (Ruddiman, 2003). The period 1720–1800 could still be considered as a reference period for pre-industrial levels of greenhouse gas emissions and global temperature (Hawkins et al., 2017). As shown by data from ice core samples, air concentrations of greenhouse gasses started to increase thereafter, slowly in the first decades, but at an accelerating rate since 1830 (MacFarling Meure et al., 2006; Schmidt et al., 2011). Not long before, in 1781, James Watt patented the steam engine condenser, which enabled to efficiently convert energy from fossil fuels (at that time mostly coal) into engine power. Soon this revolutionary technology found its way from the UK to the mainland via Belgium, where in the southern part (Wallonia) the coal mining industry expanded rapidly in the areas around Liège and Charleroi around 1820–1830 (Evans and Rydén, 2005). Also in Flanders, the northern part of Belgium, fossil-fuel dependent industry developed quickly during the 19th century, and this generally without taking measures to protect human health and the environment (De Winne, 1903). Flanders and surrounding areas including Wallonia, southern UK, northern France, the Netherlands and western Germany thus became the first region where SO_2 air concentrations exceeded natural background levels. In 1850, Western Europe accounted for the majority of global non-shipping SO_2 emissions, followed by North America as a second important emitter during the decades thereafter (Stern, 2005). The contribution of other regions initially increased slowly, but quickly gained momentum after the second World War (Stern, 2005). Global SO_2 emissions peaked, considering high uncertainties in the estimates, somewhere between 1970 and 1990 and then began to plummet (Stern, 2006; Smith et al., 2011). In Europe, SO_2 emissions peaked in the 1980s (Figure 1.1) and were then reduced by a factor 8–9 during the period until 2014 following the implementation of emission control measures included in the Helsinki protocol (1985) and the Oslo protocol (1994) (Mylona, 1996; Schöpp et al., 2003; Granier et al., 2011; European Environment Agency, 2017). In Flanders, SO_2 emissions (mainly from industrial

sources, energy production, households and traffic) were gradually reduced with 87% between 1990 and 2015 (Figure 1.2) (VMM, 2011, 2016a).
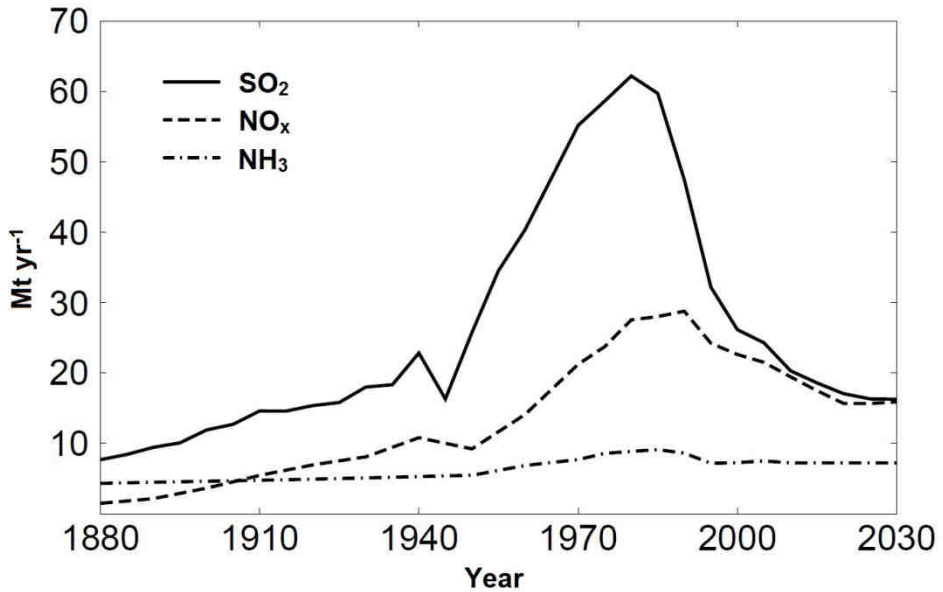
Figure 1.1 Temporal development (1880–2030) of European emissions of SO_2, NO_x and NH_3 in Mt yr^{-1} (Schöpp et al., 2003).

With regard to anthropogenic inorganic N emissions, the invention of the Haber-Bosch process in 1913 was a breakthrough. This chemical process allowed to convert non-reactive nitrogen gas (N_2) into reactive N (NH_3), that could be used as a fertilizer for food production. Anthropogenic reactive N production increased about 7-fold between 1890 and 1990 (Galloway and Cowling, 2002), while global inorganic N emissions (NO_x and NH_3) tripled between 1860 and 1990 (Figure 1.1) and further increased in the following two decades (Schöpp et al., 2003; Galloway et al., 2004; Granier et al., 2011). The implementation of emission abatement measures included in the Sofia protocol (1998) and the Gothenburg protocol (1999) reduced the emissions of NO_x and NH_3 in Europe by about 1/2 and 1/3, respectively, between 1980 and 2014 (Granier et al., 2011; European Environment Agency, 2017). In Flanders, where inorganic N emissions (NH_3 mainly from agricultural sources, NO_x mainly from traffic and industrial sources, see Table 7.2) range among the highest levels recorded in Europe, emissions were reduced at a similar rate for NO_x (47%) and at a higher rate for NH_3 (52%) between 1990 and 2015 (Figure 1.2) (VMM, 2011, 2016a).
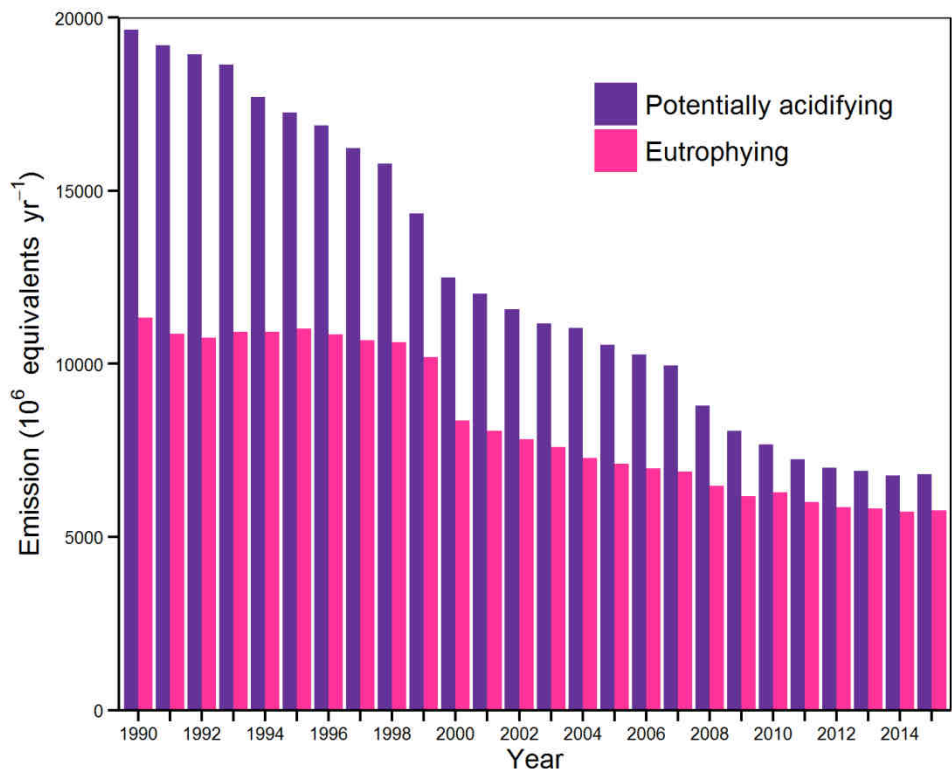
Figure 1.2 Evolution of potentially acidifying (SO_2 + NO_x + NH_3) and eutrophying (NO_x + NH_3) emissions in Flanders between 1990 and 2015 (VMM, 2011, 2016a).

The decreasing emissions of SO_2, NO_x and NH_3 resulted in declining air concentrations of pollutants and in a decrease in eutrophying and potentially acidifying depositions by 45% and 60%, respectively, in Flanders between 1990 and 2016 (Figure 1.3) (VMM, 2017).
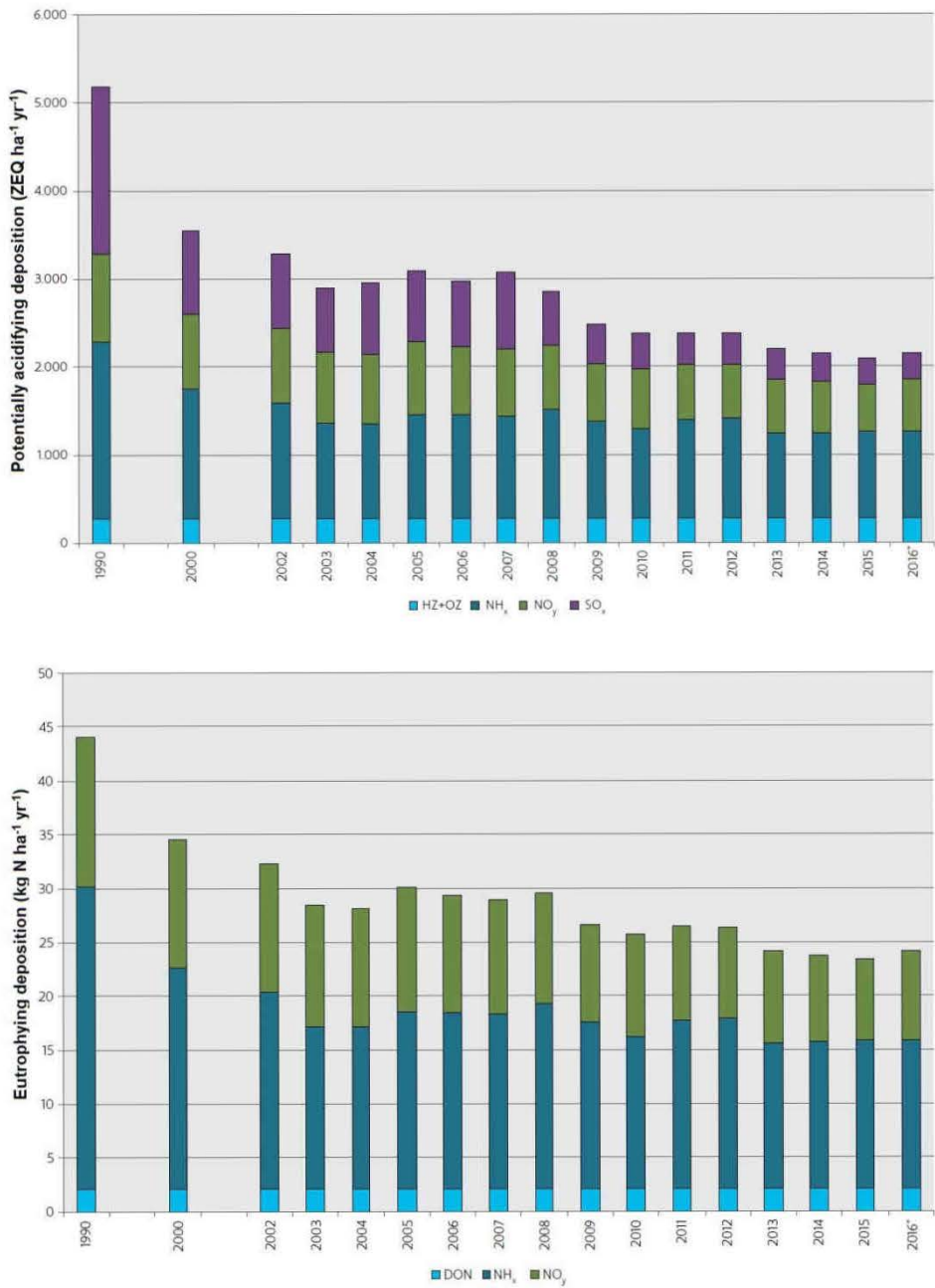
Figure 1.3 Evolution of potentially acidifying and eutrophying depositions in Flanders, as calculated with the VLOPS17 model (VMM, 2017). For halogen acids (HZ), organic acids (OZ) and DON the deposition was assumed to be constant through time. *: Data for 2016 are provisional.

1.2   **Impact of atmospheric deposition on forest ecosystems**

Adverse effects of atmospheric deposition on forest ecosystems were first reported in the 1960s (Odén, 1967) and widely received attention when atmospheric deposition was found to be an important driver of forest dieback (Ulrich et al., 1979). The dominant harmful chemical compounds in atmospheric deposition are sulphate (SO_4^{2-}) and inorganic N (NH_y and NO_y), which affect the forest soil and the vegetation through two strongly interrelated processes, i.e. acidification (by SO_4^{2-} and inorganic N) and eutrophication (with N).

1.2.1   Mechanisms

Atmospheric constituents interact with forest canopies through several processes, including wet deposition by rain or snow, sedimentation (gravimetric fall) of particles, impaction of aerosols, fog, mist and cloud droplets, absorption of gasses (e.g. NH_3, SO_2) on wet surfaces (foliage, bark, wet snow) or inside stomata on the cuticle of leaves and needles, and reemission (Ulrich, 1983). For practical reasons deposition processes are often grouped in two categories from the view point of the depositing compound, i.e. wet and dry deposition (Ulrich, 1983).

Forests are efficient sinks for atmospheric pollutants. The high leaf area index (LAI) and complex vertical structure of the vegetation create a turbulent structure of air above and within forest canopies, whereby forests capture 2–3 times more atmospheric deposition than open vegetation types (Fowler et al., 1989). In forest edges deposition is even up to two times higher than in the centre (> 100 m from the edge) (Wuyts et al., 2008; Wuyts et al., 2009). This is of particular importance in Flanders, where the forest area is highly fragmented and forests typically have sharp, steep edges (Tack et al., 1993). The rate of deposition depends on many factors, including the reactivity of compounds, atmospheric mixing ratios, the wetness and acidity of deposition surfaces (foliage, branches) and atmospheric turbulence (Fowler et al., 1999; Neirynck et al., 2007).

A part of the compounds of dry deposition is retained by the canopy (canopy uptake), and a part is washed out during rain events (canopy leaching). These processes are collectively referred to as canopy exchange (Mayer and Ulrich, 1977; Lindberg et al., 1986). Canopy uptake has been observed for protons (H^+) and inorganic N, of which more for ammonium (NH_4^+) than for nitrate (NO_3^-) (Neirynck et al., 2007; Adriaenssens et

al., 2011; 2012a; 2012b). Canopy leaching concerns mostly base cations, i.e. calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}) and sodium (Na^+), and likewise chloride (Cl^-) and weak organic acids (Lindberg et al., 1986; Staelens et al., 2008; Thimonier et al., 2008; Adriaenssens et al., 2013). Atmospheric deposition also interacts with other living and dead parts of the trees, including bark, buds, flowers and pollen, the latter being a possible source of nitrite (NO_2^-) and dissolved organic carbon (DOC) (Thimonier et al., 2008; Bright et al., 2009; Verstraeten, 2017). Tree inhabiting biota, including nitrifying bacteria (Guerrieri et al., 2015), phytophagous insects (Pitman et al., 2010) and epiphytic mosses and lichens (Conti and Cecchetti, 2001) also interact with atmospheric deposition. Finally, partial evaporation of the intercepted precipitation increases the concentration of dissolved compounds (Miralles et al., 2010). As a result, the chemical composition of water percolating through the canopy (throughfall) and flowing down the stem of trees (stemflow), differs considerably from the chemical composition of rainwater (Eaton et al., 1973).

Part of the throughfall and stemflow ("stand precipitation") reaching the forest floor may be lost through surface runoff, which is particularly important in forests on highly impermeable soil in hilly or mountainous terrain (Bonell, 1993). In Flanders most forests are located on well-drained soils on level or gently sloping terrain and most stand precipitation infiltrates in soil. The chemical composition of this soil solution reflects the equilibrium between atmospheric deposition, soil physico-chemical (mineral weathering, sorption-desorption, cation exchange, etc.) and biological processes (uptake, immobilisation, mineralisation, root exudation, etc.) (Smith, 1976; Mulder and Cresser, 1994; Schwesig et al., 2003; Scott and Rothstein, 2014).

1.2.2   Eutrophication with nitrogen

Under natural background emissions, throughfall and stemflow make up an important return of nutrients to the forest floor (Parker, 1983). In temperate forests, N is generally the limiting nutrient, but elevated supply of inorganic N through atmospheric deposition can accelerate natural soil acidification processes (see section 1.2.3) and lead to eutrophication with N (further denoted as eutrophication), i.e. enrichment of the ecosystem with inorganic N, inducing a variety of changes in N processes and ecosystem properties (Figure 1.4) (Driscoll et al., 2003b; Lebauer and Treseder, 2008; Zhu et al., 2015). If the amount of deposited inorganic N chronically exceeds the combined nutritional demands of plants and microbes, forests may become N saturated (Nihlgård,

1985; Aber et al., 1989). The process of N saturation is particularly complex and the impacts are not confined to the forest ecosystem, but are propagated to groundwater, surface water and finally back to the atmosphere (the so-called N cascade) (Galloway, 1998; Galloway et al., 2003).
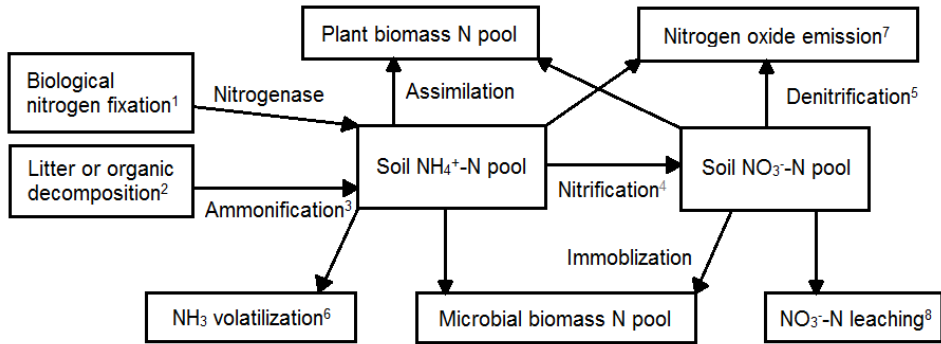
Figure 1.4 Nitrogen pools and key processes of nitrogen cycle in forest ecosystems. N input: 1, 2; N transformation: 3–5; N output: 6–8. Taken from Zhu et al. (2015).

The conceptual framework for the ecosystem response to elevated N deposition is still subject of debate and has been revised several times during the past decades (Aber et al., 1989; Gundersen, 1991; Aber et al., 1998; Galloway et al., 2003; Emmett, 2007; Lovett and Goodale, 2011; Niu et al., 2016). In the original conceptual model the transition from a N limited to a N saturated forest is a progressive three-sequential stage process (Aber et al., 1989; Aber et al., 1998; Galloway et al., 2003). Inorganic N addition is assumed to change the N status of forest ecosystems, and to implicate long-lasting effects (Vitousek et al., 1997; Aber et al., 2003). However, the conceptual model as proposed by Aber et al. (1989) in fact represents just one possible case, namely ecosystems with both strong vegetation and soil sinks (Lovett and Goodale, 2011). Lovett and Goodale (2011) proposed a more general conceptual model of N saturation (kinetic N saturation), wherein the fate of inorganic N added to the forest ecosystem is controlled by each component of the N cycle simultaneously and depending on individual site characteristics, including the size and quality of soil carbon pools, ground vegetation composition and hydrological conditions. This framework is believed to better describe the observed patterns of ecosystem responses to inorganic N deposition. Unlike the framework of Aber et al. (1989), however, it cannot predict temporal patterns of various processes unless the relative importance of those processes is known (Lovett and Goodale, 2011). Each of the existing frameworks thus has strengths and weaknesses

(Niu et al., 2016). The integration of substrate-based mechanisms into biogeochemical models, especially observed response functions of N processes with substrates from experimental studies, has the potential to improve model capability to predict future N dynamics in terrestrial ecosystems in response to N deposition (Niu et al., 2016).

Elevated N deposition represents a fertilization of the forest, initially resulting in increased tree growth and productivity together with elevated atmospheric CO_2 assimilation (Magnani et al., 2007; Ciais et al., 2008; Solberg et al., 2009; Bontemps et al., 2011; Büntgen et al., 2013; Pretzsch et al., 2014). In this phase, N addition could also lead to higher aboveground and belowground C sequestration in forests (Magnani et al., 2007; de Vries et al., 2009; de Vries et al., 2014b). However, increased productivity also implies higher nutrient demand, and in case the soil nutrient supplying capacity cannot meet these demands, eutrophication could lead to deterioration of tree mineral nutrition (Jonard et al., 2015; Talkner et al., 2015; Waldner et al., 2015). When the amount of N deposition chronically exceeds the capacity for N uptake and retention by plants, soils and microbes, forests may gradually become N saturated over the years (Aber et al., 1989; Zhu et al., 2015). In N saturated forests, inorganic N has predominantly negative effects on the trees, including damage to fine roots resulting in reduced fine root biomass and root length, reduced tree stability, higher and potentially toxic N concentrations in leaves and enhanced sensitivity to secondary stress factors such as frost, drought and fungal diseases (Nihlgård, 1985; Erisman and de Vries, 2000). Because of these reasons, tree growth is expected to stagnate or even decrease under N saturated conditions (Gundersen, 1991; Kint et al., 2012; de Vries et al., 2014a; Etzold et al., 2014; Silva et al., 2015). Furthermore, eutrophication causes shifts in the species community composition of arbuscular and ectomycorrhizal fungi and negatively affects their biodiversity (Lilleskov et al., 2002; van Diepen et al., 2007; Cox et al., 2010; Kjøller et al., 2012; Suz et al., 2014; De Witte et al., 2017). Similarly, eutrophication leads to declining species richness and changes in the composition of the ground vegetation and the communities of epiphytic mosses and lichens by promoting nitrophilic and acid-tolerant species at the expense of species that prefer more neutral and N-poor soils, as well as the animals and microorganisms that depend on them (Vitousek et al., 1997; Emmett, 2007; Fenn et al., 2008; Van Landuyt et al., 2008; Bobbink et al., 2010; de Vries et al., 2014a; Dirnböck et al., 2014; Giordani et al., 2014; van Dobben and de Vries, 2017). Finally, eutrophication leads to increased NO_3^- leaching (Aber et al., 1989; MacDonald et al., 2002; Zhu et al.,

2015) and may eventually pollute the local groundwater and surface waters (Dise and Wright, 1995).

Since the implementation of N abatement protocols in the 1990s, N depositions started to decrease in European forests, with on average 1.3–1.8 % yr^{-1} between 2000 and 2010, but only in high-deposition areas (Waldner et al., 2014). Despite these moderate reductions, N saturation will likely have long-lasting impacts on forests, because N may have accumulated in the soil (Ladanai et al., 2007) and certain ecosystem compartments (ground vegetation, ectomycorrhizal fungi, ...) respond to cumulative rather than to actual N dose and thus react slowly to decreases in N deposition (Novotný et al., 2016; Stevens, 2016; Payne et al., 2017).

At long-term forest monitoring sites across Europe, the critical limit for N saturation of 1 mg N L^{-1} in soil solution (see section 1.2.5), was frequently exceeded in about one third to half of the forests during the past two decades, indicating that N saturation is widespread in Europe (Iost et al., 2012; Waldner et al., 2015).

1.2.3   Acidification

Soil acidification is a natural phenomenon governed by several factors/processes, including climate (precipitation surplus), soil buffer capacity, mineral composition and weathering, soil organic matter (SOM) build-up and mineralization, vegetation (plant uptake, rooting depth), etc. (Table 1.1). All these processes either produce or consume protons (H^+), and the H^+-budget determines whether a soil acidifies or alkalinizes (van Breemen et al., 1983; van Breemen et al., 1984; Binkley and Richter, 1987).

Atmospheric deposition of (dissolved) sulphuric acid (H_2SO_4) and nitric acid (HNO_3) and NH_y originating partially from anthropogenic emissions of SO_2, NO_x and NH_3 (see section 1.1.1), is an important external source of H^+ in forest soils and thus accelerates soil acidification (Van Miegroet and Cole, 1984; Reuss et al., 1987; Ulrich, 1991; Vitousek et al., 1997).

Table 1.1 Proton producing and consuming processes in terrestrial and aquatic ecosystems (van Breemen et al., 1984).

Proton-producing processes	Proton-consuming processes
Atmospheric input	Drainage
Assimilation of cations	Mineralization of cations
Mineralization of anions	Assimilation of anions
Dissociation of acids	Protonation of anions
Oxidations	Reductions
Precipitation (reverse weathering) of cations	Weathering of metal oxide components
Weathering of anionic components	Precipitation (reverse weathering) of anions

Most forests in Flanders are located on acidic sand, sandy loam or silt loam soils, with only limited to moderate buffer capacity and a current pH-H_2O often as low as 3.5 to 4.5 (Ronse et al., 1988), i.e. as a result of past acidification. Since this acidic pH is below the bicarbonate buffer range incoming additional acidity can only be buffered by base cations (Ca^{2+}, K^+, Mg^{2+} and Na^+) held at clay surfaces or in soil organic matter, or by aluminium (at this acidic pH mostly Al^{3+} and more limited quantities of $Al(OH)^{2+}$ and $Al(OH)_2^+$) (Reuss and Johnson, 1986; Ulrich, 1991; Tipping et al., 2002). Proton formation in forest soils hence leads to the mobilisation and depletion of base cations from the soil exchange complex, followed by leaching (Reuss et al., 1987; van Breemen, 1991; Driscoll et al., 2001; Driscoll et al., 2003a). When the rate of base cation leaching chronically exceeds their inputs from atmospheric deposition and mineral weathering, the base saturation (BS) and acid neutralizing capacity (ANC) of the inorganic soil fraction permanently decreases, which is defined as soil acidification through atmospheric deposition (van Breemen et al., 1983).

Neutralisation of protons by Al^{3+} leads to mobilisation and leaching of Al^{3+} (Reuss et al., 1987). At a pH < 5.5 the concentrations of Al^{3+} in soil solution may reach phytotoxic levels (Al-toxicity) (Crane et al., 2007), potentially leading to root damage (Godbold et al., 2003; Vanguelova et al., 2007b), reduced nutrient uptake by the trees (and thus higher NO_3^- concentrations in soil solution and acceleration of N saturation) and symptoms of nutrient deficiency (particularly Ca^{2+} and Mg^{2+}) including needle loss, yellowing and reduced growth (DeHayes et al., 1999; Alewell et al., 2000; Driscoll et al., 2003a; de Wit et al., 2010; Sullivan et al., 2013). Acid-sensitive organisms, including deep burrowing earthworms and certain herbaceous plant species, disappear with increasing acidification (Verstraeten, 2013; Thomaes, 2014).

1.2.4   Disruption of dissolved organic matter cycling

Dissolved organic matter (DOM) is defined as the continuum of organic compounds passing a filter with a certain pore size (mostly 0.45 µm) and dissolved organic carbon (DOC) and nitrogen (DON) are the carbon and nitrogen, respectively, included in the DOM (Sleutel et al., 2009). DOM plays an important role in forest C cycling and contributes to C sequestration in mineral soils (e.g. Neff and Asner, 2001; Buurman and Jongmans, 2005). It is a highly dynamic soil organic C pool and facilitates the transport and/or bioavailability of nutrients and pollutants, including N, phosphorus (P), S and trace metals (Qualls et al., 1991; Kalbitz et al., 2000). It also forms a major pathway for C transfer from terrestrial to aquatic ecosystems, and provides a significant indirect source of CO_2 emission to the atmosphere of about 1.7 Pg C yr^{-1} (Figure 1.5) (Freeman et al., 2001; 2004; Cole et al., 2007; Battin et al., 2009; Ciais et al., 2013; Lapierre et al., 2013; Regnier et al., 2013).

Acidification and eutrophication negatively affect forest soil microbial activity, leading to reduced rates of decomposition of litter and SOM and increased soil C sequestration (Berg, 2000; Janssens et al., 2010). Acidification and N saturation often reduce the concentrations of DOC and DON in soil solution and hence diminish DOC and DON leaching (Ronse et al., 1988; McDowell et al., 2004; Evans et al., 2012), because soil solution pH controls the solubility of DOM through protonation of functional groups, i.e. higher solubility at higher pH (Kalbitz et al., 2000), and controls soil microbial activity, which is responsible for SOM decomposition and thus DOM production (Guggenberger and Zech, 1994; Kalbitz et al., 2000). OM solubility also depends on soil solution ionic strength (the sum of the concentration of each ion in solution multiplied by its valence squared:

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$$

with c_i the molar concentration of ion i (mol L^{-1}) and z_i the charge number of that ion) (Tipping and Hurley, 1988; Kalbitz et al., 2000; Haaland et al., 2010). Particularly under acidic conditions (pH < 4.2) Al^{3+} may contribute strongly to ionic strength and form organo-metal complexes with DOM, which could then be adsorbed to the soil, again lowering OM solubility (Kalbitz et al., 2000).
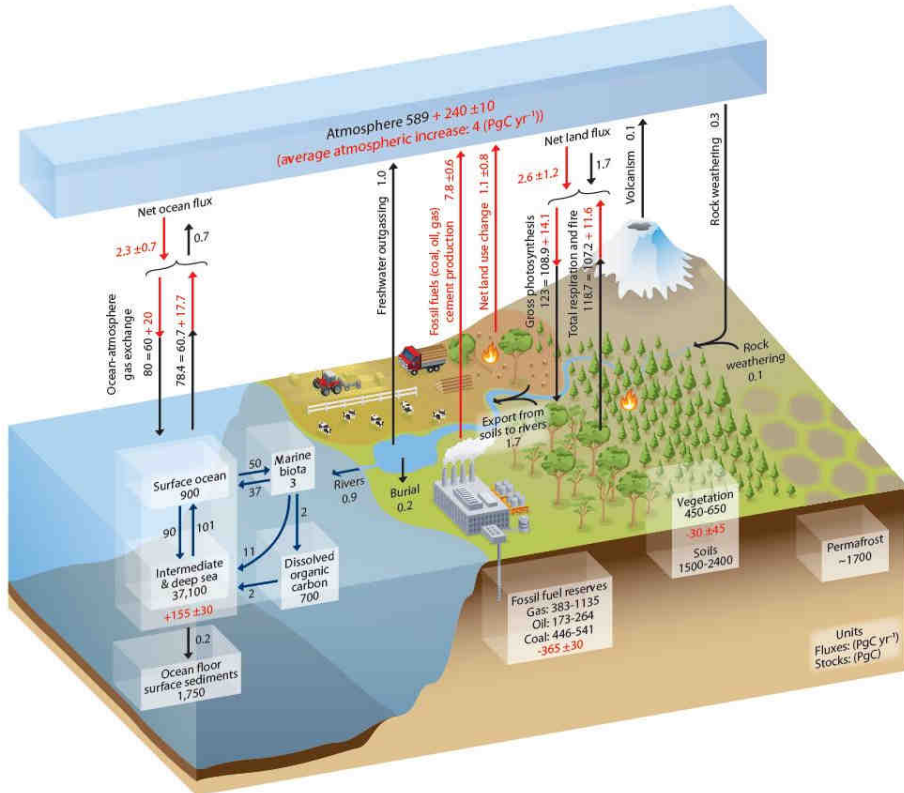
Figure 1.5 Simplified schematic of the global carbon cycle. Numbers represent reservoir mass, also called 'carbon stocks' in Pg C (1 Pg C = 1015 g C) and annual carbon exchange fluxes (in Pg C yr^{-1}). Black numbers and arrows indicate reservoir mass and exchange fluxes estimated for the time prior to the Industrial Era, about 1750. Red arrows and numbers indicate annual anthropogenic fluxes averaged over the 2000–2009 time period. These fluxes are a perturbation of the carbon cycle during Industrial Era post 1750. Uncertainties are reported as 90% confidence intervals. Taken from Ciais et al. (2013).

The control of soil solution pH and ionic strength on OM solubility makes that trends in DOC concentrations and fluxes are indicative for changes in soil acidity and N status and thus can be used to evaluate the impact of atmospheric depositions and the effectiveness of emission reduction measures. Accordingly, simultaneous positive long-term trends of DOC concentrations in stream waters and the soil solution of highly acidified forests across Europe, Canada and the US have been explained mainly by the overall decline of non-marine SO_4^{2-} depositions and subsequent initial chemical recovery of the soil solution (de Wit et al., 2007; Monteith et al., 2007; Oulehle and Hruška, 2009; Vanguelova et al.,

2010; Borken et al., 2011; Oulehle et al., 2011; Evans et al., 2012; Johnson et al., 2013; Driscoll et al., 2016; Sawicka et al., 2016).

Contrary to DOC, there is still little long-term data on DON concentrations and vertical fluxes in temperate forests under recovery from acidification, mainly because monitoring of DON was only recently introduced in forest monitoring networks. Although N-containing organic building blocks (proteinaceous or heterocyclic-N) are also comprised in the DOC (Qualls and Haines, 1991; Michalzik et al., 2001; Wu et al., 2010b), it is not clear to what extent DON concentrations follow trends in DOC. Oulehle et al. (2011) observed parallel trends in soil solution DOC and DON of a spruce forest showing acidification recovery in the Czech Republic. Vanguelova et al. (2010) found that trends in DON did not always follow positive trends in DOC at 10 ICP Forests Level II sites in the UK. It should be noted though, that both studies were shorter than nine years identified as minimum for distinguishing clear trends in DOM (Waldner et al., 2014).

1.2.5   Critical loads and limits

The concept of critical loads and critical limits is commonly used to assess the potential impact of acidification and/or eutrophication on forest ecosystem health. Critical loads and limits are defined as quantitative estimates of an exposure to deposition loads or levels above which significant harmful effects on specified sensitive elements of the environment occur according to current knowledge (Nilsson and Grennfelt, 1988). An overview of critical N and Al loads and limits for temperate forest ecosystems is given in Table 1.2.

According to Fenn et al. (2008) species loss of ground vegetation could be expected above 10–15 kg N ha^{-1} yr^{-1}, as deduced for coniferous forests in California. More recently, similar empirical critical loads for inorganic N deposition were deduced for European forests, and were in the range of 5–15 kg N ha^{-1} yr^{-1} for coniferous woodland and 10–20 kg N ha^{-1} yr^{-1} for broadleaved deciduous woodland (Bobbink and Hettelingh, 2011). Suz et al. (2014) proposed an empirical critical load range of 9.5–13.5 kg N ha^{-1} yr^{-1} for shifts in the communities of ectomycorrhizal fungi (EMF) in European oak forests. For epiphytic lichens in European forests, Giordani et al. (2014) deduced a critical load of 2.4 kg N ha^{-1} yr^{-1}, which is slightly lower than the 3.1 kg N ha^{-1} yr^{-1} proposed for epiphytic lichens in Californian coniferous forests (Fenn et al., 2008).

Critical limits for the concentration of N in soil solution were defined by UNECE (2004) for particular effects, including vegetation changes (2.5–4 mg N L^{-1} in coniferous forests, 3.5–6.5 mg N L^{-1} in deciduous forests), nutrient imbalances (0.2–0.4 mg N L^{-1}), elevated N leaching and N saturation (1 mg N L^{-1}), damage to fine root biomass/root length (1–3 mg N L^{-1}) and sensitivity to frost and fungal diseases (3–5 mg N L^{-1}). The ratio between DON and dissolved inorganic nitrogen (DIN) in soil solution, DON:DIN, is often used as an indicator for N saturation in forests (Park and Matzner, 2006; Williams et al., 2004; 2001), as are the ratios of DON to total dissolved nitrogen (TDN), DON:TDN, and DOC to NO_3^-, DOC:NO_3^- (Currie et al., 1996; Sleutel et al., 2009; Taylor and Townsend, 2010).

Critical limits for impacts of acidity were defined for damage to fine roots, reduced tree stability (risk for windthrow), inhibited root growth and growth reductions, based on the molar ratio of Ca^{2+} to total aluminium (Al_{tot}) in soil solution (Ca:Al_{tot}) (Cronan and Grigal, 1995; Vanguelova et al., 2007a) or the molar ratio of base cations (BC = Ca^{2+} + K^+ + Mg^{2+}) to Al_{tot} (BC:Al_{tot}) (Sverdrup and Warfvinge, 1993; UNECE, 2004). As long as the ANC of the soil solution has a negative value (ANC < 0), forest ecosystems are assumed to be in a progressive state of acidification (Holmberg et al., 2001; UNECE, 2004).

Elemental concentrations in foliage and their ratios also are often used to evaluate tree nutritional status, providing an indication of N and nutrient availability (biotic N status). Tree species specific critical limits have been proposed to evaluate whether nutrients are in excess or deficient (van den Burg and Schaap, 1995; Mellert and Göttlein, 2012).

Table 1.2 Overview of critical loads and limits (based on the concentrations in soil solution) commonly used to evaluate whether N or Al is in excess in temperate forest ecosystems. All ratios are molar ratios (mol/mol).

Criterion	Effect	Forest type	Reference
Critical loads			
10–15 kg N ha^{-1} yr^{-1}	Ground vegetation species loss	Coniferous (US)	Fenn et al. (2008)
5–15 kg N ha^{-1} yr^{-1}	Ground vegetation species loss	Coniferous (Europe)	Bobbink and Hettelingh (2011)
10–20 kg N ha^{-1} yr^{-1}	Ground vegetation species loss	Deciduous (Europe)	Bobbink and Hettelingh (2011)
9.5–13.5 kg N ha^{-1} yr^{-1}	Shifts in EMF communities	European oaks	Suz et al. (2014)
2.4 kg N ha^{-1} yr^{-1}	Epiphytic lichens species loss	Coniferous (US)	Fenn et al. (2008)
3.1 kg N ha^{-1} yr^{-1}	Epiphytic lichens species loss	All types (Europe)	Giordani et al. (2014)
Critical limits			
Eutrophication			
2.5–4 mg N L^{-1}	Vegetation changes	Coniferous	UNECE (2004)
3.5–6.5 mg N L^{-1}	Vegetation changes	Deciduous	UNECE (2004)
> 0.2 mg N L^{-1}	Nutrient imbalances	Coniferous	UNECE (2004)
> 0.4 mg N L^{-1}	Nutrient imbalances	Deciduous	UNECE (2004)
> 1 mg N L^{-1}	Elevated N leaching / N saturation	All types	UNECE (2004)
1–3 mg N L^{-1}	Damage to fine root biomass/root length	All types	UNECE (2004)
3–5 mg N L^{-1}	Sensitivity to frost and fungal diseases	All types	UNECE (2004)
DIN:DON < 0.5 (molar)	N saturation stage 0	All types	Williams et al. (2004)
DIN:DON 0.5–2 (molar)	N saturation stage 1	All types	Williams et al. (2004)
DIN:DON > 2 (molar)	N saturation stage 2	All types	Williams et al. (2004)
DOC:NO$_3^-$ < 5.22 (molar)	N saturated	All types	Taylor and Townsend (2010)
Acidification			
Ca:Al$_{tot}$ ≤ 1 (molar)	50% risk of Al stress	All types	Cronan and Grigal (1995)
Ca:Al$_{tot}$ ≤ 0.5 (molar)	75% risk of Al stress	All types	Cronan and Grigal (1995)
Ca:Al$_{tot}$ ≤ 0.2 (molar)	100% risk of Al stress	All types	Cronan and Grigal (1995)
BC:Al$_{tot}$ < 0.6 (molar)	Growth reduced to 80% of unaffected	*Fagus sylvatica* L., *Quercus robur* L.	Sverdrup and Warfvinge (1993)
BC:Al$_{tot}$ < 1.2 (molar)	Growth reduced to 80% of unaffected	*Pinus* sylvestris L.	Sverdrup and Warfvinge (1993)

1.3   **Long-term monitoring of air pollution effects on forests**

1.3.1   Europe and beyond

The deterioration of forest ecosystem health in the vicinity of emission sources of SO_2 in central and eastern Europe initiated the implementation of air pollution abatement policies and measures in Europe, starting with the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) (1979, Geneva). In 1985, the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) was established under the Working Group on Effects (WGE) within the LRTAP Convention. ICP Forests designed and facilitated the installation of two large-scale monitoring networks (officially Level I in 1986 and Level II in 1994), with the initial objective to collect and compile data on the condition of forest ecosystems across the UNECE region, and monitor their health and performance (Sanders et al., 2016). At present, 42 countries (27 EU member states) are cooperating in these large-scale monitoring networks, in accordance with the two major aims of ICP Forests (Sanders et al., 2016):

- Aim I: To provide a periodic overview of the spatial and temporal variation of forest condition in relation to anthropogenic and natural stress factors (in particular air pollution) by means of European-wide and national, large-scale representative monitoring on a systematic network (Level I).
- Aim II: To gain a better understanding of cause-effect relationships between the condition of forest ecosystems and anthropogenic as well as natural stress factors (in particular air pollution) by means of intensive monitoring on a number of selected permanent observation plots spread over Europe, and to study the development of important forest ecosystems in Europe (Level II).

In total about 6000 Level I plots based on a 16 × 16 km grid and 800 Level II plots were established, representing the major forest types of Europe.

1.3.2   Flanders

Flanders participated actively in the ICP Forests programme since the very beginning and cooperates in both the Level I and Level II networks.

The plots of the Level I network were systematically selected according to a grid. Originally, 10 plots were part of the international 16 × 16 km Level I survey. From 1995 on, the Level I survey was performed on a 4 × 4 km grid, with 62 additional (regional) plots (72 plots in total). Nowadays data from 8 Flemish level I plots is yearly reported to ICP Forests, together with results from the regional survey (Cools et al., 2016; Sioen et al., 2016).

The Level II plots were installed in well pre-screened forest stands in the most important forest types in Flanders. The Level II network is thus not spatially representative for the area of Flanders, but it is assumed to reliably represent important forest types. The Level II network originally counted 12 plots that were installed in 1987–1991, one of which was abandoned in 2002. Of the 11 remaining plots, five are operated as "core" plots (see section 2.1 for a detailed description). The six other Level II plots are operated as "additional" plots. A detailed description of the additional plots was published in Cools et al. (2016). All research presented in this thesis is based on the monitoring data collected in the five Flemish Level II core plots.

The monitoring programme in the Level II plots consists of surveys carried out on a regular basis (Table 2.4). In the five Level II core plots an intensive monitoring programme is conducted, including continuous monitoring of atmospheric deposition, soil solution chemistry, soil water content, litterfall chemistry and air concentrations of NH_3. The plots in Gontrode and Brasschaat are equipped with a measuring tower operated by, or in cooperation with the universities of Ghent and Antwerp, respectively. In the six additional Level II plots only a limited number of surveys is conducted (Table 2.4).

1.4   Aim and outline of the thesis

Emission control policies and practical measures implemented since the 1980s for SO_2 and since the 1990s for inorganic N resulted in a substantial reduction of anthropogenic acidifying and eutrophying emissions and depositions in Flanders (see section 1.1.2). As shown by experiments with reduced N and S input in the Netherlands and the cessation of experimental N addition in the US, this could lead to recovery of soil solution chemistry (Boxman et al., 1995; Boxman and Roelofs, 2006; McNulty et al., 2017). However, at present it is unclear whether the emission reductions had any beneficial effects on the condition of temperate forests in Flanders, which underwent progressive soil acidification between 1950 and 2000 (Ronse et al., 1988; De Schrijver et al., 2006) and showed clear

signs of N saturation (De Schrijver et al., 2004). The main aim of this thesis was to evaluate if there has been a response of temperate forest ecosystems in Flanders to reductions in nitrogenous and potentially acidifying emissions. More specifically, the objectives were to evaluate recent evolutions in soil solution chemistry and tree mineral nutrition in Flemish forests, in order to check whether the rates of soil solution acidification and N saturation are slowing down or recovery has started. Improving mechanistic insights into the processes associated with soil solution acidification and eutrophication is an enormous challenge, given the complexity that is inherently associated with a large number of interacting factors. However, improving these insights would only be possible with large additional efforts. In this thesis we aimed at an in-depth analysis of existing long-term and unique monitoring datasets. Whilst such analysis necessarily leads to the formulation of assumptions on the processes responsible, testing these assumptions was outside of the scope of this thesis, but presents interesting hypotheses for further more mechanistic research, as suggested also in the General discussion section. Figure 1.6 provides a schematic overview of the outline of this thesis.

To address the objectives of this thesis we formulated several hypotheses. Testing these hypotheses requires long-term data on the environmental (abiotic) conditions in Flemish forests and the nutritional status (biotic) of the trees. In the five Flemish Level II core plots atmospheric depositions, soil solution chemistry and foliar chemistry are monitored continuously or at regular time intervals (Table 2.4). With time series spanning ten to more than 20 years and consisting of high-quality data collected according to the guidelines of the ICP Forests manual (ICP Forests, 2016), this dataset provided the basic information required for this study. In Chapter 2 the Level II core plots are described in detail with regard to site history, species composition, stand structure, hydrology and soil characteristics. Chapter 2 also contains a description of the datasets selected for this study and of the materials and methods used to further extend these datasets with new data over the course of this study.

Chapter 3 deals with the impact of declining atmospheric deposition on soil solution chemistry in Flemish forests. Long-term trends (1994–2010) of the depositions of eutrophying and potentially acidifying inorganic N and S compounds and BC are evaluated. Because potentially acidifying and eutrophying emissions and depositions showed decreasing trends in Flanders (see section 1.1.2) this is the 1st hypothesis that was tested:

> 1) Potentially acidifying depositions decreased in Flemish forests during the study period.

The results are discussed in relation to empirical critical loads for ground vegetation and sensitive epiphytic lichens. Also the parallel trends of SO_4^{2-} and inorganic N compounds, BC, Al_{tot} and pH in soil solution are analysed. Regarding the expected decreasing trends in depositions and the possible impact on soil solution, this is the 2nd hypothesis that was tested:

> 2) The decreasing depositions lowered the elemental concentrations in soil solution, leading to a better condition with regard to critical loads and levels.

The concentrations in soil solution are discussed in relation to critical limits for the BC:Al_{tot} ratio and for the ANC. Soil water fluxes are calculated for each plot and finally, an ion budget is discussed for stand depositions (inputs) and soil solution fluxes (outputs) of SO_4^{2-} and inorganic N compounds.

In Chapter 4 the impact of air-borne or canopy-derived DOC on forest soil solution DOC is examined over an 11-year period (2002–2012). Trends of DOC concentrations and fluxes in open field precipitation, stand precipitation and soil solution are evaluated. Because several studies found an overall increasing trend in DOC concentrations in surface waters and also in the soil solution at a number of intensive forest monitoring sites in high-deposition areas as the result of decreasing SO_4^{2-} depositions (see section 1.2.4), this is the 3rd hypothesis that was tested:

> 3) Soil solution DOC concentrations and fluxes increased during the study period.

Furthermore, the seasonal patterns of DOC concentrations and fluxes are analysed with a focus on the impact of air-borne or canopy-derived DOC on DOC in soil solution, since the current knowledge about this topic is limited. Because a number of studies found a relationship between throughfall DOC and soil solution DOC moderated by the activity of phytophagous insects in the canopy (Michalzik and Stadler, 2005; Pitman et al., 2010), this is the 4th hypothesis that was tested:

> 4) Changes in soil solution DOC concentrations and fluxes were related to changes in air-borne or canopy-derived DOC.

In Chapter 5 the trends and patterns of DON concentrations and fluxes in deposition (open field precipitation and stand precipitation) and soil solution are evaluated. Published long time series on DON concentrations in soil solution are rare and little information is currently available about whether trends in DON follow trends in DOC (see section 1.2.4). Since N-containing organic building blocks (proteinaceous or heterocyclic-N) are also comprised in the DOC, this is the 5th hypothesis that was tested:

> 5) Concentrations and fluxes of DON in the deposition and soil solution followed the DOC trends.

The results are discussed in relation to abiotic soil condition (pH, SO_4^{2-} concentration, Al^{3+} concentration and ionic strength) (2005–2013). Also trends and patterns of the molar ratio of DOC and DON, DOC:DON, are evaluated. Since N-rich DOM compounds generally have a lower reactivity with Fe and Al hydroxides, a pH control on DON solubility is probably smaller than for DOC. Hence, this is the 6th hypothesis that was tested:

> 6) Recovery from acidification disproportionally favours DOC dissolution compared to DON, resulting in an increase in the DOC:DON ratio over time.

In Chapter 6 the evolution of forest N status is evaluated by two indicators based on the soil solution concentrations of DOC, DON, TDN and NO_3^-, more particularly the molar DON:TDN ratio (2005–2014) and the molar DOC:NO_3^- ratio (2002–2014) and their relation with DIN deposition. Regarding the observed decreasing trends in potentially acidifying and eutrophying depositions and trends in soil solution (decreasing NO_3^-, increasing DOC, DON and pH) resulting from the research presented in the previous chapters, this is the 7th hypothesis that was tested:

> 7) The DON:TDN ratio and thus the DOC:NO_3^- ratio increased over the past decade, but increased DON and DOC mobilization due to concomitant recovery from acidification renders these shifting ratios only partly indicative for the actual improvement in forest N status.

Furthermore, two indicators based on the foliar concentrations of N, P and BC (the N:P ratio and the molar BC:N ratio) are used to evaluate forest N status (1999–2013). Considering the above, this is the 8th hypothesis that was tested:

8) The foliar N:P ratio and BC:N ratio decreased and increased, respectively, as a consequence of lowered soil mineral N availability.

The general discussion in Chapter 7 focuses on two important questions: 1) Is air pollution abatement policy in Flanders on target with respect to forest protection?, and 2) Do we already see a recovery from acidification and N eutrophication in Flemish forests and on what term, if at all, could we expect a substantial recovery? For the first question the depositions in the five Level II plots are discussed in relation to 2010-target and 2030-target values for deposition included in (inter)national legislation (NEC-directive 2001/81/EG, VLAREM II) and critical loads for ground vegetation, epiphytic lichens and ectomycorrhizal fungi. The depositions are also compared with national emission data (VMM, 2011, 2016a), using recently collected data up to 2015. The evolution of the molar NH_4^+:NO_3^- ratio is discussed in a European context. The second question is more philosophic and is used as a background to discuss how forests in Flanders are expected to evolve in the future, based on the current trends and socio-economic developments. Furthermore, implications for policy and management are given, as well as a number of suggestions and directions for further research. Also the strengths, weaknesses and uncertainties of the methods used are discussed. Finally, the main conclusions of this work are listed.

Change of abiotic conditions

Inorganic compounds

Chapter 3
- Are atmospheric depositions decreasing?
- Is this reflected in soil solution chemistry?
- Are critical loads and limits still exceeded?

Biotic response

Nitrogen status

Chapter 6
- Is the N status of forests improving?

\# indicators for soil solution   \# indicators for tree mineral nutrition

Organic compounds

Chapter 4
- Are DOC concentrations increasing?
- Is DOC leaching increasing?

Chapter 5
- Are DON concentrations and fluxes increasing?
- Is DOC:DON changing?

Figure 1.6 Outline of the thesis.

2 MATERIALS AND METHODS

2.1 Study area

Five plots of the ICP Forests intensive monitoring network (Level II) in Flanders (northern part of Belgium) were included in this study (Figure 2.1). Flanders has a moderate Atlantic climate with a mean annual precipitation of 852 mm and mean temperature of 10.5 °C (long-term averages for 1981–2010 for the meteorological station of Uccle, http://www.meteo.be). The five intensive monitoring plots are 'core' plots of the ICP Forests Level II network (http://icp-forests.net/). The plots are located in protected Natura 2000 forest habitats (or in development) (https://www.natura2000.vlaanderen.be/) and are also part of the Long-Term Ecosystem Research (LTER) network in Europe (http://www.lter-europe.net/).
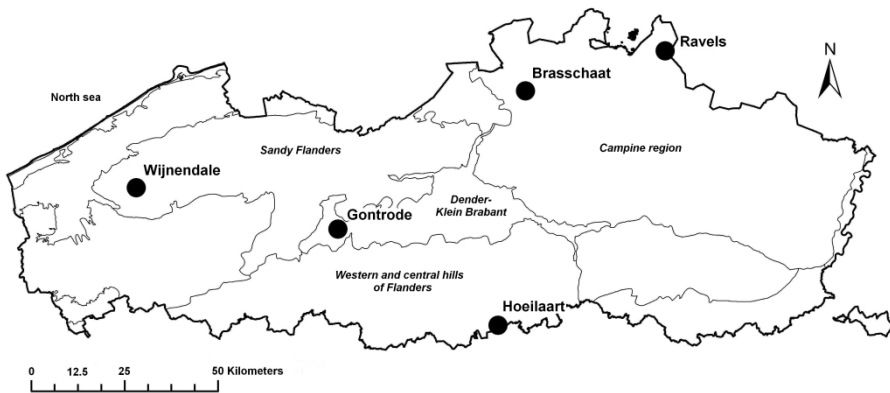
Figure 2.1 Location of the five intensive forest monitoring plots in relation to ecoregions (Sevenant et al., 2002) in Flanders.

The five Level II plots were installed in 1987–1991 (circular plots, with an area of 0.25 ha each, surrounded by a buffer zone of 0.25 ha). Relevant site characteristics are listed in Table 2.1, detailed soil characteristics in Table 2.2 and soil solution characteristics in Table 2.3. A short description of each Level II plot including pictures is given below.

Table 2.1 Characteristics of the five Level II plots in Flanders. Mean annual temperature (MAT) and precipitation (MAP) are long-term averages for the nearest meteorological station (1981–2010, Royal Meteorological Institute of Belgium, www.meteo.be). Basal area was calculated from a full survey (DBH ≥ 5 cm) in 2009–2010. Throughfall and stemflow are expressed as the average proportion of open field precipitation. The term 'ancient forest' stands for permanently forested (as far as known) at least since 1775.

Plot	Coordinates N	E	Elevation (m)	MAT (°C)	MAP (mm)	Tree species	N2000 Type	Planting year	Former use	Basal (m² ha^{-1})	Throughfall (%)	Stemflow (%)	Groundwater range (m)
Coniferous forests													
RAV	51°24'07''	05°03'15''	35	10.4	887	*Pinus nigra subsp. laricio* var. *Corsicana* Loud.	9190*	1930	heath	44.9	68.3		1.5–2.5
BRA	51°18'28''	04°31'11''	14	10.8	882	*Pinus sylvestris* L.	9190*	1929	heath	29.2	78.6		1.2–2.3
Deciduous forests													
WIJ	51°04'11''	03°02'14''	31	11.0	867	*Fagus sylvatica* L.	9120	1935	arable	36.5	62.0	14.7	0.9–2.3
GON	50°58'31''	03°48'15''	26	10.6	786	*Quercus robur* L.*, Fagus sylvatica* L.	9130	1918	ancient forest	31.9	71.8	3.2	1.5–1.8
HOE	50°44'45''	04°24'47''	129	10.7	854	*Fagus sylvatica* L.	9120	1909	ancient forest	28.9	70.9	5.8	>30

*: in development

Table 2.2 Soil characteristics of the five Level II plots: soil type according to IUSS Working Group (IUSS Working Group WRB, 2007), sampling depths, morphogenetic horizons, C and N concentrations (g kg^{-1}), C:N ratio, pH-CaCl$_2$ (molarity 0.01 M), cation exchange capacity (CEC) (cmol$_c$ kg^{-1}) and base saturation (BS) (%) for the forest floor layers (OF, OH or OFH) and five fixed depth layers of the mineral soil. Humus types were defined in 2007 (Zanella et al., 2011). Mean dry bulk density of the fine earth (BD) (kg m^{-3}) and soil texture data (USDA textural triangle) are given for the mineral soil layers (clay, silt and sand fractions in mass %). Soil samples were collected in 2004 and analysed using methods of the ICP Forests manual, part X (Cools and De Vos, 2016).

Plot	Soil type	Humus Type	Sampling Depth	Morphogenetic Horizon	C	N	C:N	pH-CaCl$_2$	CEC	BS	BD	Clay 0–2 µm	Silt 2–63 µm	Sand 63–2000 µm
			(cm)		(g kg^{-1})	(g kg^{-1})	(–)	(–)	(cmol$_c$ kg^{-1})	(%)	(kg m^{-3})	(%)	(%)	(%)
RAV	Endogleyic Folic Brunic	mor	-6.6 to -0.8	OF	491	15.1	33	2.5	23	36				
	Albic Arenosol (Dystric)		-0.8–0	OH	366	10.5	35	2.3	26	16				
			0–5	Ap/E	38.7	1.43	27	2.9	4.6	11	1242	2.3	10.2	87.5
			5–10	Ap/E	24.2	0.90	27	3.0	3.8	7.6	1378	0.9	12.6	86.5
			10–20	Ap/E	19.2	0.83	23	3.1	3.6	7.4	1271	0.7	11.9	87.4
			20–40	Bhs	17.9	0.83	21	3.4	3.3	8.2	1322	3.0	12.0	85.0
			40–80	B, Bg1	4.55	<0.5	–	4.1	1.7	15	1355	1.4	12.3	86.3
BRA	Endogleyic Brunic	mor	-5.2–0	OFH	492	16.2	30	2.7	25	42				
	Albic Hypoluvic		0–5	Ap1	18.9	1.07	18	3.1	2.2	18	1397	2.0	7.0	91.0
	Arenosol (Dystric)		5–10	Ap1	10.8	0.60	18	3.2	1.8	15	1455	1.9	4.7	93.4
			10–20	Ap1	8.49	0.57	15	3.3	1.7	16	1463	1.8	5.9	92.3
			20–40	Ap1, Ap2	7.15	0.50	14	3.4	1.6	17	1493	1.0	6.1	92.8
			40–80	E, Bg1, Bg2	3.17	<0.5	–	3.6	1.5	18	1500	1.6	5.3	93.1

Table 2.2 continued.

Plot	Soil type	Humus Type	Sampling Depth	Morphogenetic Horizon	C	N	C:N	pH-CaCl$_2$	CEC	BS	BD	Clay 0–2 µm	Silt 2–63 µm	Sand 63–2000 µm
			(cm)		(g kg^{-1})	(g kg^{-1})	(–)	(–)	(cmol$_c$ kg^{-1})	(%)	(kg m^{-3})	(%)	(%)	(%)
WIJ	Endogleyic Folic	mor	-8.0 to -2.1	OF	541	22.0	25	2.7	31	42				
	(Brunic, Humic,		-2.1–0	OH	304	13.7	22	2.7	25	23				
	Hyperdystric, Arenic)		0–5	A1	119	5.73	21	2.5	7.3	32	761	–	–	–
			5–10	A2	36.6	1.97	19	2.7	4.2	14	1370	3.3	24.7	72.0
			10–20	A2	18.5	1.17	16	3.0	3.5	11	1314	3.8	23.8	72.5
			20–40	A3	18.1	1.00	18	3.3	3.1	10	1367	3.6	21.5	74.9
			40–80	Bhg, Cgc	7.19	0.70	10	3.6	3.0	11	1390	5.9	21.9	72.2
GON	Luvic Planosol	moder	-6.2–0	OFH	579	17.5	25	3.6	–	–				
	(Albic, Ruptic, Dystric,		0–5	A	441	17.4	20	2.9	17	23	1036	–	–	–
	Siltic, Clayic)		5–10	B	52.2	2.57	17	2.9	15	20	1233	9.5	50.6	39.9
			10–20	B, 2B	29.7	1.70	17	3.0	12	15	1515	11.0	48.2	40.8
			20–40	2B, 2Bg	16.7	0.97	12	3.3	14	21	1483	24.5	46.0	29.5
			40–80	2Bg, 3Bg	8.26	0.70	7.8	3.5	23	61	1411	47.5	36.6	15.9
HOE	Albic Cutanic Alisol	moder	-3.0–0	OFH	359	15.5	23	3.1	24	81				
	(Fragic, Abruptic,		0–5	A	43.0	2.53	17	3.3	6.3	16	1147	10.6	85.9	3.6
	Hyperdystric, Siltic)		5–10	Bh	19.3	1.17	17	3.5	4.3	13	1321	5.3	90.7	4.0
			10–20	E	10.3	0.73	14	3.8	3.8	11	1445	14.4	81.8	3.8
			20–40	Bt	5.73	0.55	10	3.8	4.6	8.9	1470	13.5	81.3	5.2
			40–80	Btx1	2.95	0.55	5.4	3.8	5.2	16	1509	19.1	76.9	4.0

Table 2.3 Range (min–max) in pH, electronic conductivity (EC), and the concentrations of DOC and major cations and anions (mg L^{-1}) in soil solution in the five Level II plots. All parameters were measured from 1994 till 2010 except DOC (1999–2010), TDN and DON (2005–2010).

Plot	Period	Sampling Depth	pH	EC	Al_{tot}	Fe_{tot}	Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-
		(cm)	(–)	(–)	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})
O horizon											
RAV	1994-2010		3.38–7.3	38–262	<0.1–1.2	<0.1–0.61	0.45–10.2	0.74–17.4	<0.1–1.9	0.92–10.6	0.9–22.4
BRA	1994-2010		3.39–7.3	27–232	<0.1–0.7	<0.1–0.61	0.39–10.4	0.4–9.95	0.1–2.5	0.7–17.4	0.9–34
WIJ	2003-2010		3.28–6.96	43–317	<0.1–0.45	<0.1–0.38	0.67–11.8	2.47–20.8	0.18–2.61	1.17–8.56	1.49–24.1
GON	1994-2010		3.57–7.1	47–319	<0.1–1.4	<0.1–1.22	1.36–17.4	2.1–23.6	<0.1–4.8	1–13.4	1.3–29.7
HOE	1994-2010		3.9–7.8	24–283	<0.1–1.3	<0.1–1.27	0.31–17.5	0.67–29.4	0.2–4.21	0.71–11.4	0.6–23
A horizon											
RAV	1997-2010	10-25	3.1–3.9	93–451	1.29–21.9	<0.1–0.96	<0.1–11.3	<0.1–5.12	0.13–2.4	2.06–20.3	1.38–32
BRA	2002-2010	15-25	3.05–3.9	109–548	0.5–11.5	0.47–1.73	0.45–7.71	0.2–5.49	0.29–2.53	2.49–22	3–38.5
WIJ	2002-2010	10-20	3.24–3.9	102–363	0.5–5.31	0.4–2.07	0.5–8.4	0.1–9.2	0.39–2.25	2.28–18.9	3.15–43.4
GON	1996-2010	10-20	3.32–6.64	102–466	<0.1–11.6	<0.1–1.71	2.12–35.3	2.7–22.4	1.02–14.7	2.45–18.7	3.9–44
HOE	2001-2010	10-15	3.78–5.32	38–183	0.5–2.97	<0.1–0.89	0.79–9.4	0.38–7.86	0.32–2.3	1.5–6.23	1.4–16.9
B horizon											
RAV	2002-2010	30-45	3.62–4.23	66–398	4.2–22.8	<0.1–0.4	0.53–5.4	<0.1–1.8	0.16–2	3.09–21.9	3.77–34.6
BRA	1994-2010	30-55	2.8–3.88	127–683	0.9–16.8	0.38–2.6	0.89–15.1	0.5–6.3	0.48–3.3	3.8–23	3.25–35.4
WIJ	1998-2010	45-70	3.4–4.42	89–529	2.35–29	<0.1–1	0.26–13.3	<0.1–5	0.26–6.6	4.02–41.3	6.23–108
GON	1999-2010	25-40	3.51–4.33	70–341	0.24–6.58	<0.1–0.9	1.4–14.7	4.7–17.9	0.52–4.72	3.24–12.6	3.7–21.4
HOE	1998-2010	20-30	3.87–5.5	32–143	0.2–3.05	<0.1–0.57	0.69–7.7	0.36–6.8	0.2–1.9	1.2–9.7	1.9–23.3
C horizon											
RAV	1994-2010	70-95	3.6–4.49	37–507	2.97–29.7	<0.1–0.3	0.21–9.6	0.11–3	<0.1–2.45	2.05–33.4	2.87–52.8
BRA	1997-2010	70-90	3.3–4.2	127–496	0.49–25.4	<0.1–1.47	0.33–9.5	0.38–3.7	0.16–4.2	3.4–27.7	3.9–48.6
WIJ	2002-2010	75-110	3.83–4.62	126–352	3.2–12.6	<0.1–0.38	0.32–6.6	0.18–1.13	0.67–3.7	7.64–34.2	12.5–77.9
GON	1994-2010	45-55	3.5–4.8	123–332	1–7.1	<0.1–0.4	2.82–17.6	2.13–11.4	1.26–6.4	3.1–17.8	4.1–46
HOE	1996-2010	35-55	4–5.41	43–156	<0.1–3.2	<0.1–0.18	1.07–10.9	0.5–3.9	0.42–2.4	2–10.5	2.5–25

Table 2.3 continued.

Plot	Period	Sampling Depth (cm)	SO_4^{2-} (mg L^{-1})	NH_4^+ (mg L^{-1})	NO_3^- (mg L^{-1})	N_{tot} (mg L^{-1})	DON (mg L^{-1})	DOC (mg L^{-1})
O horizon								
RAV	1994-2010		1.72–39.3	<0.1–15.2	0.5–47.7	2.1–23	0.09–5.47	4.7–210
BRA	1994-2010		2.61–51.8	<0.1–14	0.5–28.8	1.43–15.7	0.11–9.77	1.31–116
WIJ	2003-2010		1.92–28	<0.1–11.5	1.27–65	1.82–16.9	0.1–9.67	10.1–55
GON	1994-2010		2.96–58.4	<0.1–11.3	0.5–85.6	2.69–39	0.08–5.75	6.4–87
HOE	1994-2010		2.05–37.6	<0.1–13	0.5–115	1.66–21.3	0.33–4.58	2.18–77.2
A horizon								
RAV	1997-2010	10-25	2.94–68.5	<0.1–8	1.15–105	1.33–27.1	0.21–4.82	8.88–81
BRA	2002-2010	15-25	6.11–38.2	<0.1–0.89	0.13–75.8	1.83–16.9	0.1–4.26	9.21–71
WIJ	2002-2010	10-20	5.28–29.5	<0.1–0.6	0.16–78	0.75–8.39	0.4–3.14	9.45–66
GON	1996-2010	10-20	6.51–156	<0.1–5.85	0.5–119	6.28–26	0.23–7.27	7.44–42.4
HOE	2001-2010	10-15	3.73–16.1	<0.1–0.8	0.11–54.5	<0.1–11.5	0.06–2.47	8.6–38
B horizon								
RAV	2002-2010	30-45	4.98–40.4	<0.1–1.6	0.45–103	1.39–35.4	0.16–4.64	20.6–65.8
BRA	1994-2010	30-55	10.1–91.5	<0.1–10	2.01–169	1.32–16	0.15–2.74	14.9–81.1
WIJ	1998-2010	45-70	7.1–54.3	<0.1–5	0.14–196	<0.1–10.1	0.02–2.77	1.05–39.1
GON	1999-2010	25-40	9.18–36.5	<0.1–0.89	3.01–87.7	1.78–22.2	0.04–5.31	10–44.5
HOE	1998-2010	20-30	5.2–20.7	<0.1–2	<0.1–31.9	<0.1–5.87	0.01–1.57	2–24.1
C horizon								
RAV	1994-2010	70-95	4.69–71.5	<0.1–0.95	0.59–184	0.63–30.6	0.11–2.94	10.1–59.6
BRA	1997-2010	70-90	11.4–117	<0.1–0.5	2.47–71	0.98–14.3	0.09–2.44	10.6–47.1
WIJ	2002-2010	75-110	18.5–42	<0.1–0.44	0.11–51.3	<0.1–4.82	0.04–1.38	5.3–21
GON	1994-2010	45-55	13–57.2	<0.1–0.99	2.58–68.4	0.72–21.1	0.13–5.65	7.76–33.5
HOE	1996-2010	35-55	5.69–31.3	<0.1–0.66	0.11–33.7	0.2–7.59	0.07–1.59	2.04–35.4

2.1.1 Ravels (RAV) (nr. 14)

Level II plot nr. 14 is located in the forest 'Gewestbos Ravels-Noord' (820 ha), in the community of Ravels, in the northern Campine ecoregion of Flanders. This Level II plot constitutes the LTER-site 'Ravels forest' (LTER_EU_BE_04). The surrounding area is agricultural, with a high concentration of livestock breeding farms. The soil is a well-drained sandy soil (Arenosol) with a C:N ratio of 33–35 in the organic layer (mor humus) (Figure 2.2).

Figure 2.2 Soil profile in Level II plot Ravels (nr. 14) (photo: Nathalie Cools) with on the right side the morphogenetic horizons and their depth ranges (cm) for the upper 130 cm taken from Mikkelsen et al. (2008).

The Level II plot is located in a homogeneous Corsican pine stand (*Pinus nigra* ssp. *laricio* var. *Corsicana* Loud.), which was planted in 1930 on former heathland (Figure 2.3). The herb layer is dominated by broad buckler fern (*Dryopteris dilatata* Hoffm.), bilberry (*Vaccinium myrtillus* L.) and purple moor grass (*Molinia caerulea* (L.) Moench). A sparse understorey of silver birch (*Betula pendula* L.) and rowan (*Sorbus aucuparia* L.) is developing since several trees were thrown down by a storm in January 2007. This site is considered to be a Natura 2000 forest habitat 9190 in development.

Figure 2.3 Overview of the Level II plot Ravels (nr. 14) (photo: Arne Verstraeten).

2.1.2   Brasschaat (BRA) (nr. 15)

Level II plot nr. 15 is located in the forest 'De Inslag' (150 ha), in the community of Brasschaat, in the northern Campine ecoregion of Flanders. This plot is located within the fenced scientific zone of 2 ha which constitutes the LTER-site 'Brasschaat De Inslag' (LTER_EU_BE_001). The forest is located in a suburban area at 10 km east of the port of Antwerp, which contributes more than half of the SO_2 emissions in Flanders. The soil is a sandy soil (Arenosol) with a C:N ratio of 30 in the organic layer (mor humus). The infiltration of water is locally slowed down by clay lenses at 50–125 cm depth (Figure **2.4**).
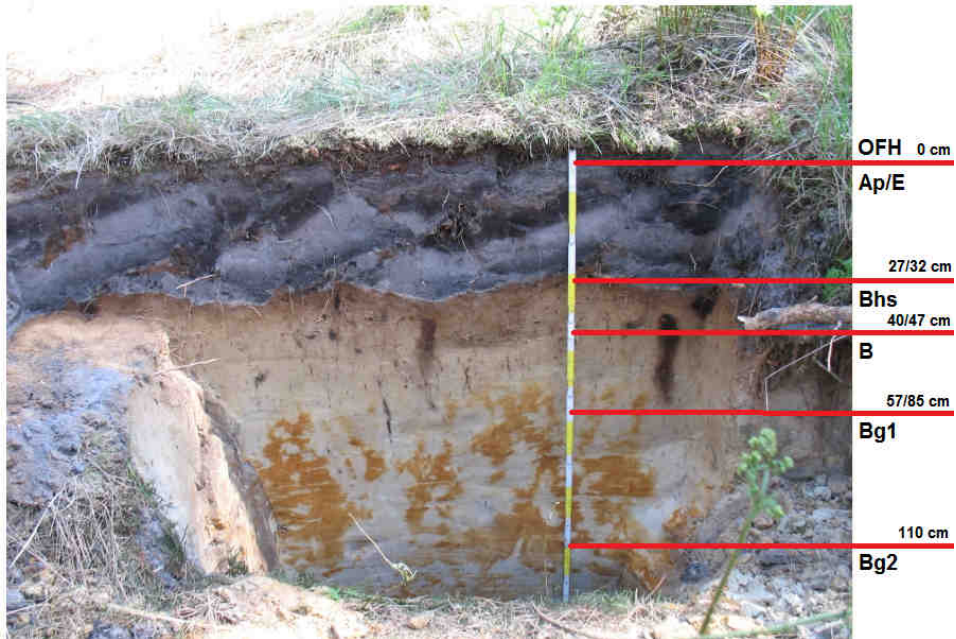
Figure 2.4 Soil profile in Level II plot Brasschaat (nr. 15) (photo: Nathalie Cools) with on the right side the morphogenetic horizons and their depth ranges (cm) taken from Mikkelsen et al. (2008).

The Level II plot is located in a homogeneous Scots pine stand (*Pinus sylvestris* L.), which was planted in 1929 on former heathland (Figure 2.5). The herb layer is dominated by *Molinia caerulea* (L.) Moench and several ferns. The stand structure is further characterized by a diverse moss layer and ingrowth of several tree and shrub species

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(*Betula pendula* L., *Frangula alnus* Mill., *Sorbus aucuparia* L., …). The site contains a 40 m high measuring tower, where meteorological variables and the air concentrations of pollutants are monitored above and below the canopy since 1995. The scientific area and the surrounding forest also function as a Belgian ICOS measuring site (www.icos-belgium.be), which is coordinated by the Research Centre of Excellence PLECO (Plant and Vegetation Ecology) of the University of Antwerp (www.uantwerpen.be/en/rg/pleco). This site is considered to be a Natura 2000 forest habitat 9190 in development.

Figure 2.5 Level II plot Brasschaat (nr. 15) with a view of the measuring tower (photos: left: Arne Verstraeten; right: Johan Neirynck).

2.1.3   Wijnendale (WIJ) (nr. 11)

Level II plot nr. 11 is located in the Wijnendale forest (181 ha) in the community of Ichtegem, in the western part of Sandy Flanders. It is an important component of the LTER-site 'Forest of Wijnendale' (LTER-EU-BE-05). The surrounding area is agricultural and consists mainly of arable land. The soil is a sandy loam soil (Umbrisol) with presence of clay below 90 cm depth, a shallow groundwater table, moderately low base saturation in the mineral soil and slightly higher base saturation in the topsoil. The mineral soil is characterized by a 60-cm thick two-layered Ap horizon, which indicates soil disturbance, probably due to the temporary conversion of forest to cropland during periods of food scarcity in the mid-19th century (Figure 2.6).
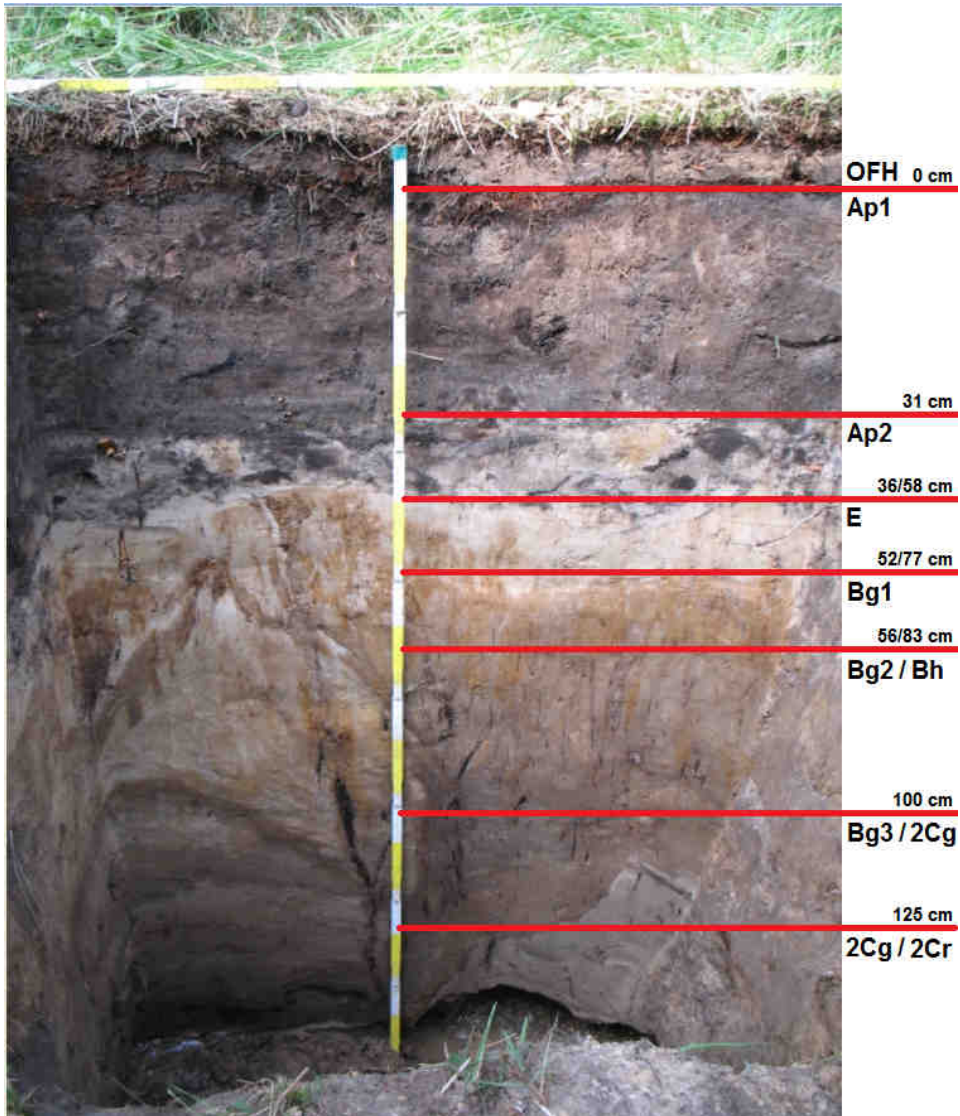
Figure 2.6 Soil profile in Level II plot Wijnendale (nr. 11) (photo: Nathalie Cools) with on the right side the morphogenetic horizons and their depth ranges (cm) taken from Mikkelsen et al. (2008).

The Level II plot is located in a homogeneous European beech stand (*Fagus sylvatica* L.), which was planted in 1935 (Figure 2.7). Since the start of the monitoring, the stand structure has been characterized by the absence of a moss layer, herb layer and

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understorey, which could be explained by the shady conditions and the thick organic layer. This site is a Natura 2000 forest habitat 9120.

Figure 2.7 Level II plot Wijnendale (nr. 11) (photo: Arne Verstraeten).

2.1.4   Gontrode (GON) (nr. 16)

Level II plot nr. 16 is located in the Aelmoeseneie forest (28.5 ha), which is the experimental forest of the University of Ghent. This experimental forest forms the LTER-site 'Gontrode – Aelmoeseneie Forest' (LTER_EU_BE_03). The forest is located in the community of Gontrode, in the Dender-Klein Brabant ecoregion. The soil consists of a silt loam to loam soil (Planosol), overlaying a mosaic of tertiary clayey and sandy deposits with high base saturation starting at 50 cm depth (Figure 2.8).
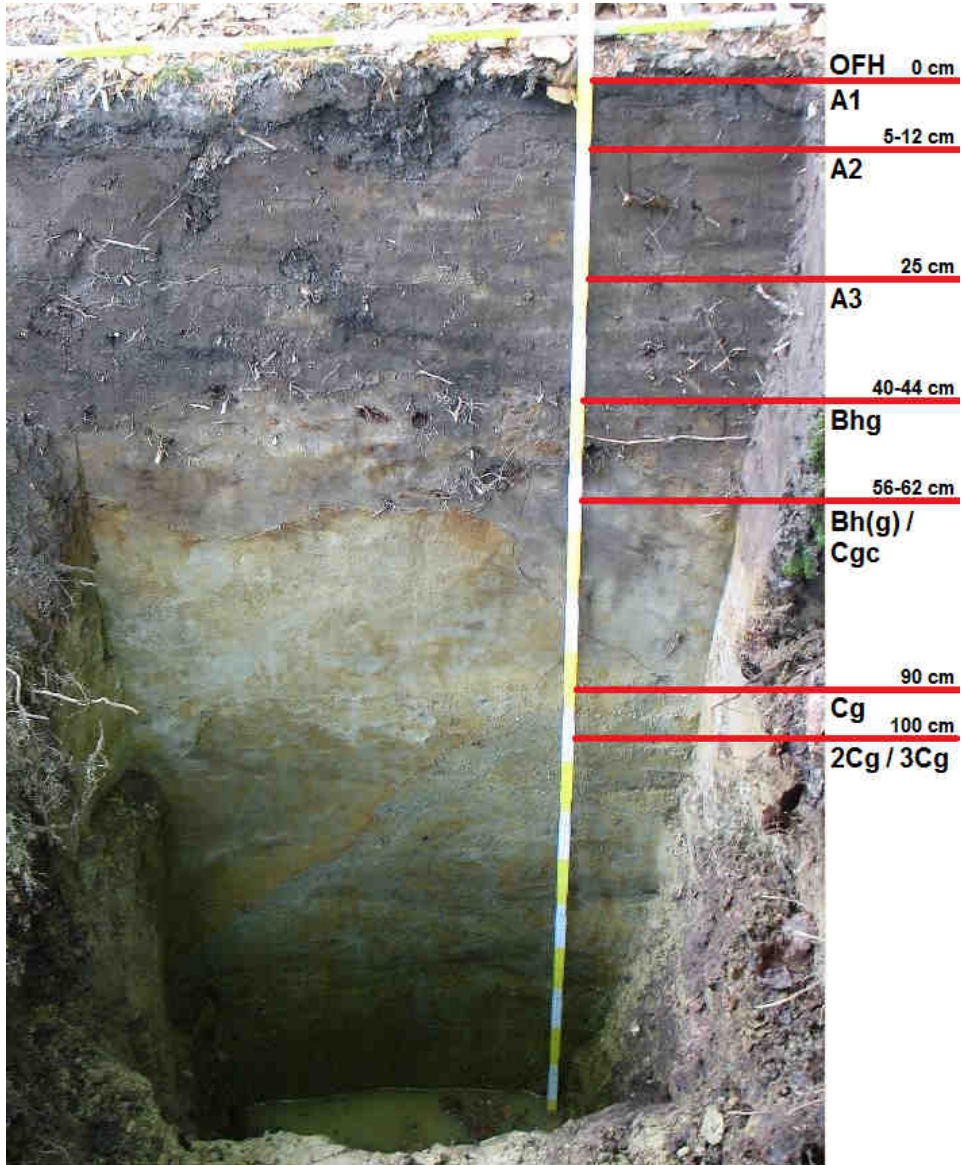
Figure 2.8 Soil profile in Level II plot Gontrode (nr. 16) (photo: Nathalie Cools) with on the right side the morphogenetic horizons and their depth ranges (cm) taken from Mikkelsen et al. (2008).

The Level II plot is located in a mixed forest stand, dominated by common (pedunculate) oak (*Quercus robur* L.) and European beech (*Fagus sylvatica* L.), and further containing European ash (*Fraxinus excelsior* L.), larch (*Larix* spp.) and sycamore maple (*Acer pseudoplatanus* L.). The main tree layer was planted shortly after the first World War in an ancient woodland site (Figure 2.9). The herb layer is moderately developed and consists of bramble (*Rubus fruticosus* L.) and a limited number of typical forest plant species (e.g. *Polygonatum multiflorum* (L.) All.). About 10 years ago the invasive *Lamium galeobdolon* subsp. *argentatum* entered the plot via the north side, where it is locally dominant. The understorey is rather dense and consists mainly of common hazel (*Corylus avellana* L.), sycamore maple and rowan (*Sorbus aucuparia* L.). The Level II plot is located in a fenced scientific area (1.83 ha) that contains a 35-m high measuring tower, where meteorological variables and tree phenology and physiology are monitored. The scientific area is operated by the Forest & Nature Lab (ForNaLab) (www.ugent.be/bw/dfwm/en/research/fornalab) and the Laboratory of Plant Ecology (www.plantecology.ugent.be) of the University of Ghent. This site is a Natura 2000 forest habitat 9130.

Figure 2.9 Level II plot Gontrode (nr. 16) with a view of the measuring tower (photos: left: Arne Verstraeten; right: Arthur De Haeck).

2.1.5 Hoeilaart (HOE) (nr. 21)

Level II plot nr. 21 is located in the Sonian forest in the community of Hoeilaart, in the central hills of Flanders. This plot constitutes an important component of the LTER-site 'Sonian Forest' (LTER_EU_BE_02), that covers the whole forest complex (4400 ha). The forest is surrounded by residential areas near the south-eastern border of the city of Brussels, and is crossed by several highways. The soil is loamy, with moderately low base saturation and deep groundwater table (> 30 m) (Figure 2.10).
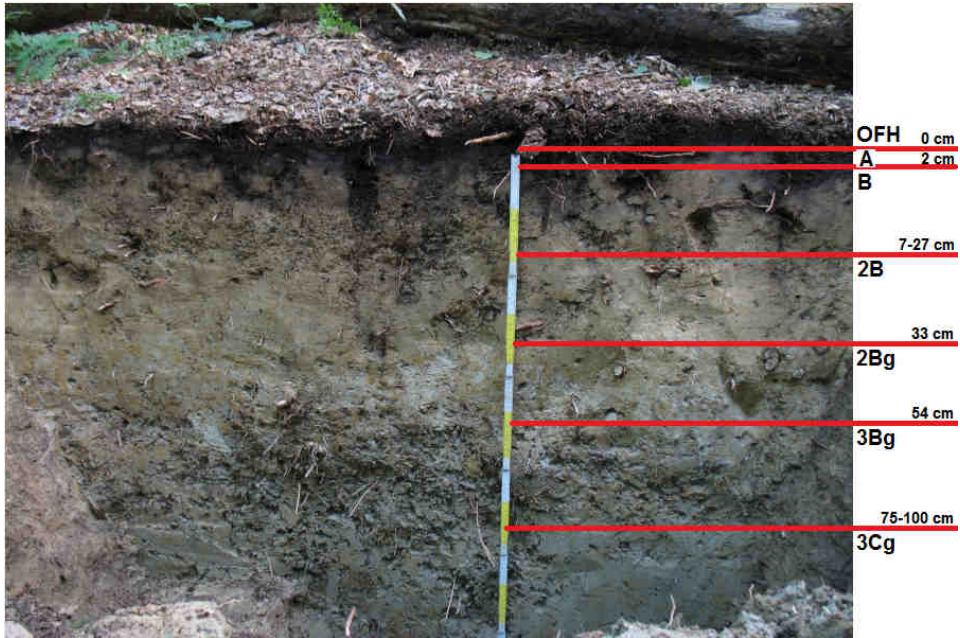
Figure 2.10 Soil profile in Level II plot Hoeilaart (nr. 21) (photo: Nathalie Cools) with on the right side the morphogenetic horizons and their depth ranges (cm) taken from Mikkelsen et al. (2008).

The Level II plot is located in a homogeneous stand of European beech (*Fagus sylvatica* L.), which was planted in 1909 on an ancient woodland site (Figure 2.11). The herb layer is relatively well developed and hosts several ancient forest plant species (*Hyacinthoides non-scripta* (L.) Rothm., *Hypericum pulchrum* L., *Lamium galeobdolon* (L.) L. subsp. *montanum* (Pers.) Hayek, *Luzula pilosa* (L.) Willd., *Maianthemum bifolium* (L.) F. W. Schmidt, *Moehringia trinerva* (L.) Clairv., *Oxalis acetosella* L., *Polygonatum multiflorum* (L.) All.). Since 2006, an understorey of beech and sycamore maple (*Acer pseudoplatanus* L.) started to develop in this Level II plot. This site is a Natura 2000 forest habitat 9120.

Figure 2.11 Level II plot Hoeilaart (nr. 21) (photos: Arne Verstraeten).

2.2 Sample collection and measurements

The monitoring programme in the Level II plots consists of several surveys, carried out on a regular basis (Table 2.4). All research presented in this thesis was based on the long-term datasets on deposition, soil solution chemistry and foliar chemistry. The available data series were thoroughly validated and further extended with new data over the course of this study using the standardized guidelines and methods of the ICP Forests manual (ICP Forests, 2016).

Table 2.4 Overview of the different surveys, current frequency of execution and the number of Level II core plots and additional plots where each survey is carried out (adopted from Cools et al. (2016)). Surveys from which data were used for the research presented in this thesis are shaded in grey.

Survey	Frequency	Core	Additional	Start[a]
Soil	Every 10 years	5	6	1992
Ground vegetation	Every 5 years	5	6	1988
Forest inventory	Every 5 years	5	6	1988
Growth				
- Girth bands	Before and after growing season	5	6	2007
- Point dendrometers	Continuously	1	-	2014
Crown condition	Every year	5	6[b]	1988
Deposition				
- Open field	Continuously (halfmonthly)	5	-	1993
- Throughfall	Continuously (halfmonthly)	5	-	1992
- Stemflow	Continuously (halfmonthly)	3	-	1994
Soil solution chemistry				
- Organic layer	Halfmonthly	5	-	1993
- Mineral soil	Halfmonthly	5	-	1992
Soil water content	Every 6 hours	5	-	1996
Ground water level	Halfmonthly	4	-	1999
Litterfall	Continuously (halfmonthly)	5	-	1999
Foliar chemistry	Every 2 years	5	6[c]	1988
Meteorology	Continuously	3	-	2011
LAI	Every year (summer and winter)	3	-	2009
Phenology				
- Observers	Every week (spring and autumn)	5	1	2002
- Camera's	Continuously	1	-	2014
Air pollutant concentrations				
- Passive samplers (O_3[d], NH_3)	Continuously (halfmonthly)	5	-	2009
- Monitors (O_3, NH_3, SO_2, NO_x)	Continuously	1	-	1995
Sapflow	Continuously	1	-	2014
Soil temperature	Every 6 hours	5	-	1996

[a] in this year the first measurements were conducted, but not necessarily at all plots and at the current frequency

[b] until 2009

[c] until 2007

[d] until 2011

2.2.1   Deposition sampling

Deposition sampling was done according to the guidelines of the ICP Forests manual, part IV (Clarke et al., 2016), including three different fractions: precipitation (rainfall) in the open field (since 1993) and under the canopy (throughfall) (since 1992) and water draining from the trunk of trees (stemflow) (since 1994).

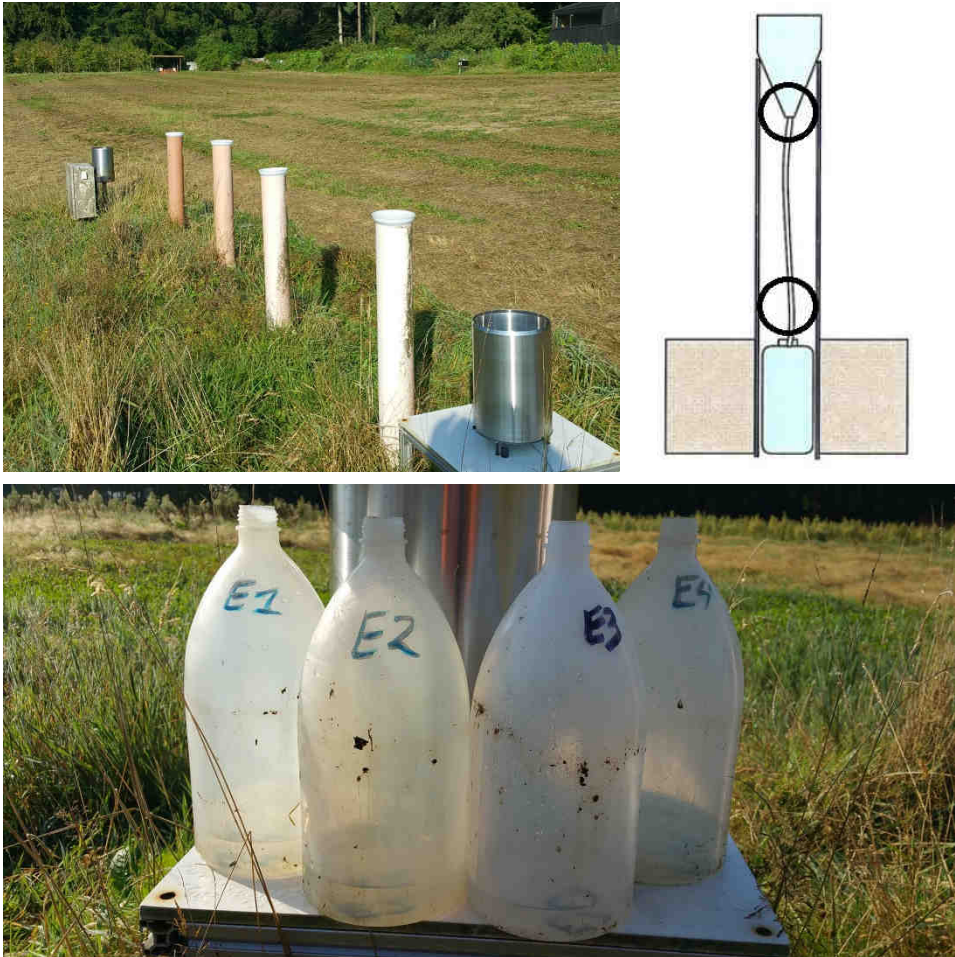Figure 2.12 View of the bulk precipitation collectors (top left) and the four partly filled sampling bottles (bottom) in the open field nearby the Level II plot in Hoeilaart (nr. 21) (photos: Yvan De Bodt), and scheme of a bulk collector (top right).

Precipitation was sampled with four bulk collectors, located in the open field (a grassland vegetation mown several times per year) nearby each Level II plot (at 200–2000 m

distance) (Figure 2.12). Bulk collectors consisted of a polyethylene funnel (14 cm Ø) placed at 1 m height on top of an orange opaque PVC tube (12 cm Ø) (Figure 2.12). The funnel was connected to a subterranean 2-L transparent polyethylene bottle by a black opaque PVC tube (2 cm Ø). The advantage of storing the collecting bottle in a soil pit was demonstrated in an experiment during an extremely hot period in the summer of 2010 at an open field site near INBO in Geraardsbergen. In this experiment light and temperature at the bottom of the collecting bottle was compared between two adjacent bulk precipitation collectors, the first with an aboveground bottle, the second with a subterranean bottle, but further identical. Water samples in the belowground bottle were protected from heat, temperature fluctuations and direct sunlight, while very large peaks and fluctuations were recorded in the aboveground bottle (Figure 2.13). As demonstrated by experiments in other countries, chemical transformations in water samples (mostly for DOC, pH, NH_4^+ and N_{tot}) may occur during storage in the field, but these changes are generally limited for short periods of up to two weeks and at temperatures below 20°C (König et al., 2013). In the five plots the average soil temperature in the upper centimetres of the mineral soil is 9.8–10.9°C and seldom reaches 20°C (Table 2.5), which means that chemical transformations in the deposition samples under field conditions likely are limited. A nylon mesh (1 mm^2 mesh size) was placed in the funnel to avoid contamination by larger particles. All collecting bottles, funnels and nylon meshes were replaced by clean material (acid-washed in the laboratory) at every sampling event.

Table 2.5 Mean, minimum, maximum and standard deviation (Sd) of soil temperature (°C) at 1–5 cm depth in the mineral soil in the five Level II plots (2011–2015).

Plot	Depth	Soil temperature			
		Mean	Min	Max	Sd
	(cm)	(°C)	(°C)	(°C)	(°C)
Coniferous forests					
RAV	1	10.5	0.0	18.9	3.8
BRA	4	10.9	1.0	20.2	3.9
Deciduous forests					
WIJ	2	10.4	2.9	17.1	3.3
GON	4	10.3	1.3	18.3	3.5
HOE	5	9.8	1.4	17.6	3.6
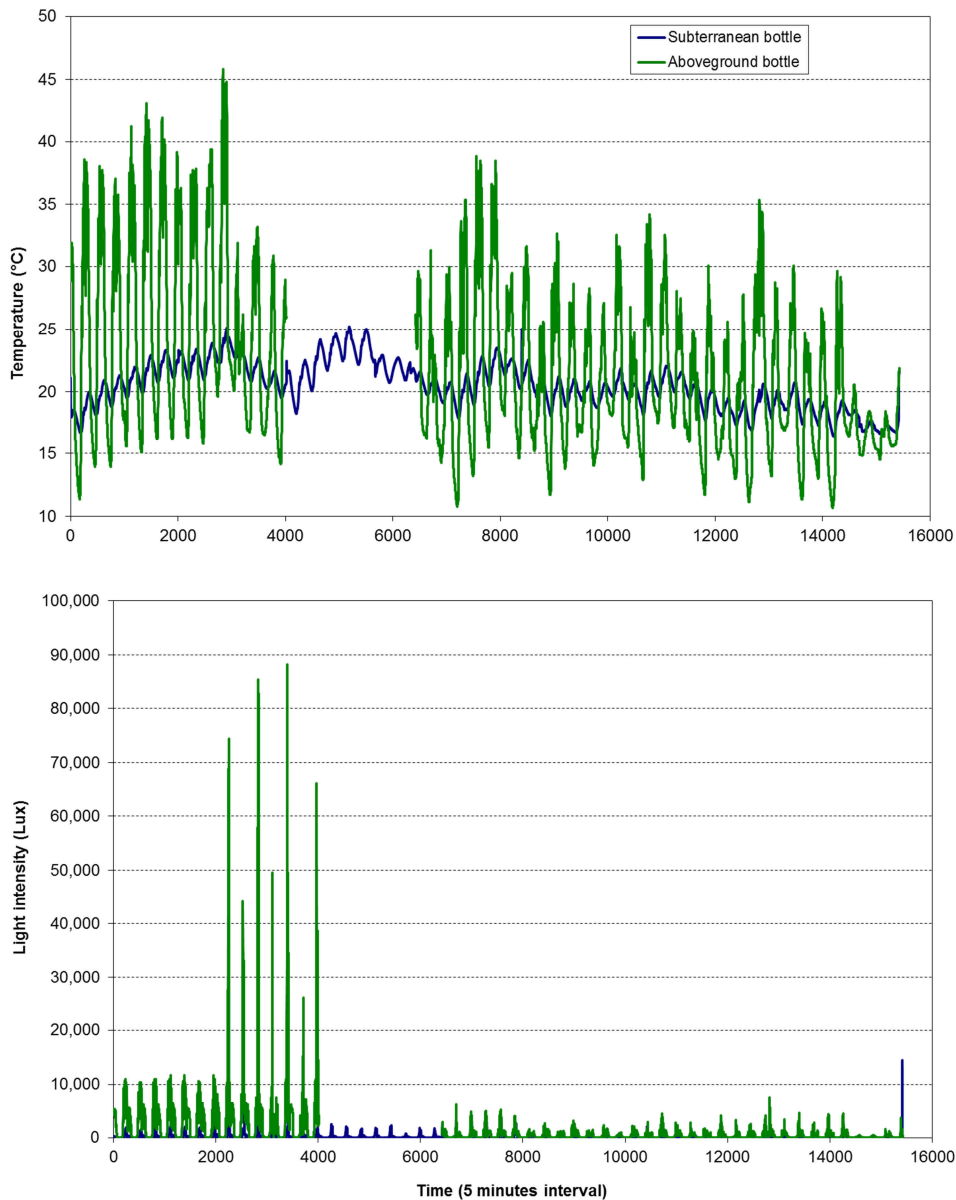
Figure 2.13 Temperature (°C) and light intensity (Lux) measured at a 5 minutes interval inside the bottle (on the bottom) of two adjacent bulk precipitation collectors with respectively a subterranean bottle and an aboveground bottle in an open field site near INBO in Geraardsbergen in the hot summer of 2010 (from 22 June till 18 August) with record air temperatures up to 33.9 °C (measured on July the 2nd at the meteorological station of Uccle, www.meteo.be) (König et al., 2013).

Throughfall was sampled in each plot with ten bulk collectors of the same type as the collectors in the open field, systematically distributed around the plot centre (Figure 2.14). At every sampling event, the volume collected in each bulk collector was determined and samples were bulked to one sample for rainfall and throughfall per plot.
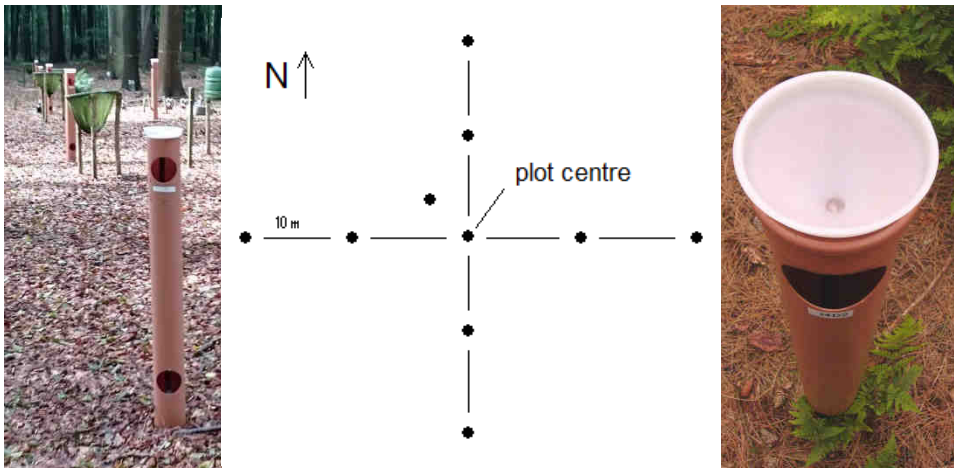
Figure 2.14 View of the throughfall collectors in Wijnendale (nr. 11) (left, photo: Yvan De Bodt), scheme of the arrangement of throughfall collectors (middle) and detail of the upper part (funnel with mesh) of a throughfall collector in Ravels (nr. 14) (right, photo: Yvan De Bodt).

Stemflow sampling was done only for *Fagus sylvatica*, because preliminary samplings had shown that stemflow for *Pinus* and *Quercus robur* was negligible (< 1 % of rainfall). In the homogeneous beech stands (WIJ, HOE) five trees of different size were selected for stemflow analysis, based on the mean (M) and standard deviation (SD) of the diameter (Ø) of all living trees in each plot in 1994 (M, M – SD, M + SD, M – 2 x SD, M + 2 x SD); in the mixed oak-beech stand (GON) three trees (M, M – 2 x SD, M + 2 x SD). Stemflow collectors consisted of flexible polyvinylchloride collars/gutters (7 cm Ø) attached horizontally to the stem at 1 m height, draining to a series of 180-L and 200-L polyethylene storage containers mounted in a cascade system using silicone tubing (Figure 2.15). The volume collected for each individual container/tree was determined at every sampling event using calibrated gauging rods (one for each type of container). Subsamples were taken from all full containers, with subsample volumes weighted to tree diameters, and bulked to one sample. Containers were emptied and cleaned in the field after every sampling event and collars/gutters were cleaned (e.g. removal of litter) and

rinsed with deionized water. The nylon meshes (1 mm2 mesh size) in the drain of collars/gutters were replaced by clean material (acid-washed in the laboratory) at every sampling event. In each plot one of the trees was equipped with an automatic tipping bucket system (UGT), allowing to store the data electronically (Figure 2.16). This device automatically collects a 1% volume weighted subsample, avoiding the use of large containers. These data were occasionally used to correct stemflow volumes in case of incidental overflow of containers, for example after abundant rainfall. Stemflow volumes, obtained from the individual trees, were scaled up to plot level using information of basal area. Immediately after sampling the deposition samples were stored in an isolated box with ice packs, wherein they were transported to the laboratory.

Because data for all deposition fractions were needed for each year, data from 1992–1993 were excluded from the data analysis.

Figure 2.15 Detail of a stem flow collar in Hoeilaart (nr. 21) (top left, photo: Yvan De Bodt), stemflow collector in Wijnendale (nr. 11) (top right, photo: Arne Verstraeten) and full containers on an icy morning in Gontrode (nr. 16) (bottom, photo: Yvan De Bodt).
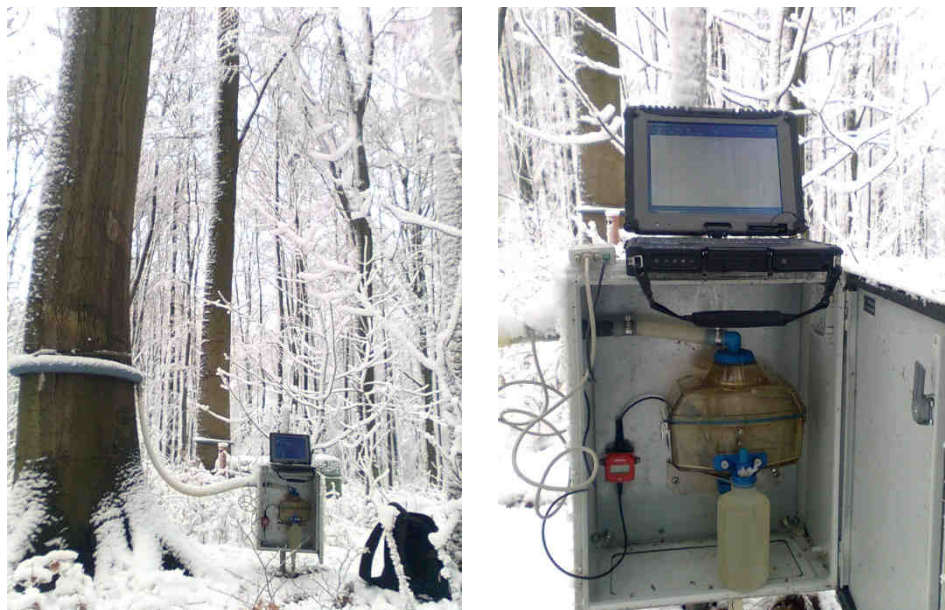
Figure 2.16 Automatic tipping bucket system (UGT) for stemflow sampling in Hoeilaart (nr. 21) (photos: Pieter Dhaluin).

2.2.2   Soil solution sampling

Samples of soil solution were collected according to the guidelines of the ICP Forests manual, part XI (Nieminen et al., 2016). Soil solution draining from the O horizon (forest floor) was sampled with two (1993–1997) and since 1997 four (RAV, BRA, GON, HOE) or six (WIJ) randomly located zero-tension lysimeters (plate lysimeters) per plot. They consisted of a 5 cm high stainless steel box covered with a nylon mesh (1 mm^2 mesh size), installed underneath the forest floor (Figure 2.17). Soil solution from the mineral soil was sampled using tension lysimeters (lysimeter 'candles') with a ceramic cup (Eijkelkamp) at two (1992–1997) and since 1997 three locations per plot (Figure 2.17). Each location was equipped with one (1992–1997) and since 1997 two to four tension lysimeters at each of three depths in the capillary zone (for practical reasons further called A, B and C horizon, although in several plots the C horizon in fact starts deeper than the range of the deepest lysimeters, which are thus in fact still in the B horizon) (Table 3.2). Each tension lysimeter was pressurized to 0.6 bar using an electric or hand vacuum pump two days before sampling. The soil solution was collected in 1–2 L bottles made from dark coloured borosilicate glass and placed in a shallow soil pit (Figure 2.17).

As explained in section 2.2.1 this protected the samples from heat and temperature fluctuations, while the shade from the canopy and the dark colour of the glass protected the samples from solar radiation, limiting the risk of chemical transformations in the samples. The collecting bottles were replaced by bottles that were acid-washed in the laboratory at least once every six months to prevent growth of algae or fungi inside the bottle. The collecting bottles were connected to the lysimeters by perfluoroalkoxy (PFA) tubing, that was replaced every 1–2 years.

Preliminary tests have shown that soil solution chemical composition could vary significantly among individual lysimeters due to spatial variation in soil characteristics, but for financial reasons, samples were bulked to one composite sample per depth per plot at every sampling event, using the entire collected volume.

Figure 2.17 Tension lysimeters in Brasschaat (nr. 15) (left, photo: Arne Verstraeten), zero-tension lysimeter in Ravels (nr. 14) (top right, photo: Arne Verstraeten) and preparation of soil solution samples (bottom right, photo: Yvan De Bodt).

Because it was the objective of this work to study the impact of depositions on soil solution chemistry, soil solution data from 1992–1993 were excluded from the data analysis, as was done for the deposition data (see section 2.2.1).

For the mineral soil, tension lysimeters were chosen because the installation of zero-tension lysimeters would create too much soil disturbance. The first tension lysimeters (1994) were installed at an angle of 45°, avoiding disturbance of the soil above the cup, but the disadvantage is that the characteristics of the soil layers above and the exact depth of the lysimeter are unknown. Therefore, tension lysimeters were placed vertically into the soil since 1997. For the O horizon was opted for zero-tension lysimeters, because there it is difficult to maintain a good contact between suction cups and the surrounding organic matter. Zero-tension lysimeters consequently collect more water than tension lysimeters in organic layers, while tension lysimeters collect more water in the mineral soil because the pressure allows to capture also capillary water together with percolating water (Nieminen et al., 2016).

It should be remarked that the ceramic cups of newly installed tension lysimeters may absorb DOC, particularly the hydrophobic fraction derived from decomposing litter (Guggenberger and Zech, 1992; Rais et al., 2006). This effect however disappears when the lysimeter is well equilibrated in the field (Guggenberger and Zech, 1992). Therefore, samples of newly installed tension lysimeters were not mixed with the samples of existing lysimeters until solute concentrations had normalized. A minimum equilibration period of six months was respected, and even longer if necessary (mostly concentrations normalized within 3–6 months). If solute concentrations did not normalize within a period of one year, or if the new lysimeter quickly lost its pressure or the retrieved sample quantity remained insufficient, it was reinstalled or, when suspected to be malfunctioning, replaced by another lysimeter. It should also be remarked that ceramic cups give good results for B and C horizons but are less suitable for A horizons, because DOC concentrations could be more variable there and a percolation volume of 300 ml is needed to reach equilibrium, which is often difficult in A horizons (Guggenberger and Zech, 1992). Besides DOC, also heavy metals could be absorbed by ceramic cups (Rais et al., 2006), but likely this problem also disappears when lysimeters are well equilibrated in the field, because the sorption capacity is limited. While ceramic cups are suitable to examine most ions and elements in solution (NO_3^-, Na^+, Cl^-, SO_4^{2-}, ...) glass cups are better to study DOC and plastic cups for heavy metals, but for financial and practical reasons it was of course impossible to work with three different tension lysimeter types,

regarding the number of replicates needed to cover spatial variability and to obtain sufficient sample volume for analysis.

Immediately after sampling the soil solution samples were stored in an isolated box with ice packs, wherein they were transported to the laboratory.

2.2.3   Sampling of needles and leaves

Sampling of fresh tree foliage (leaves or needles) was carried out biennially (uneven years) by professional tree climbers (Figure 2.18). Samples were always collected from the same five dominant trees in each plot and from the upper third of the crown (needles or leaves that developed in light), according to the guidelines of the ICP Forests manual, part XII (Rautio et al., 2016). This meant that specific branches were cut by hand wearing powder free laboratory gloves. These were immediately put in polyethylene bags, in which they were also carried down. Then a first selection of branches was made and these were stored in sealed polyethylene bags, which were transported to the laboratory in isolated boxes with ice packs.

Figure 2.18 Tree climber Wim Vancraeynest (Arbol) on his way to the canopy (left) and selection of needle samples by Luc De Geest (right) in Brasschaat (photos: Arne Verstraeten).

2.3   **Sample pre-treatment and chemical analysis**

Samples were treated and analysed as prescribed by the ICP Forests manual, part XI, XII and XIV (Clarke et al., 2016; Nieminen et al., 2016; Rautio et al., 2016). Quality control included the analysis of control samples (blanks, reference material, replicates) and participation in the ICP Forests water and foliar ring tests, according to the guidelines of the ICP Forests manual, part XVI (König et al., 2016).

2.3.1   Deposition and soil solution samples

Water samples (500-mL subsamples of each collected fraction) were kept cool during transportation, filtered (0.45 µm), stored in darkness at 4 °C and analysed within 48 hours after sampling. pH (Multi 340i-glass electrode, WTW) and conductivity (Multi 340i-Tetracon$^{®}$325, WTW) were measured on unfiltered subsamples. Concentrations of cations (Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+) and anions (Cl^-, NO_3^-, NO_2^-, SO_4^{2-}) (mg L^{-1}) were determined simultaneously using ion chromatography (Dionex ICS-3000, LOQ = 0.1 mg L^{-1}). Concentrations of DOC were determined using a TOC-analyser (Shimadzu TOC 5050A, LOQ = 0.1 mg C L^{-1}). Concentrations of total Kjeldahl nitrogen (TKN) were determined using the modified Kjeldahl (continuous flow) method (Skalar, limit of quantification, LOQ = 0.5 mg N L^{-1}). Concentrations of total aluminium (Al_{tot}) and iron (Fe_{tot}) in soil solution samples were measured with an inductive coupled plasma spectrometer (Varian Liberty Series II ICP-OES, LOQ = 0.1 mg L^{-1}).

2.3.2   Foliage samples

In the laboratory, sufficient leaves or needles were picked from the selected branches. Foliage samples were dried in an oven at 40 °C until constant weight and pulverised with a suitable mill (Retsch SM 2000). For each of the sampled trees a homogenized subsample was analysed at every sampling event. Foliar N concentrations (mg g^{-1} dry weight at 105 °C) were determined using the modified Kjeldahl method with NH_4^+-back titration (Gerhardt KB8S, LOQ = 1 mg N kg^{-1}). Foliar concentrations of P, Ca, K and Mg (mg g^{-1} dry weight at 105 °C) were determined using an inductive coupled plasma spectrometer (Varian Liberty Series II ICP-OES, LOQ = 50 mg kg^{-1}) after microwave digestion with HNO_3/H_2O_2.

2.4 **Calculation of drainage fluxes**

Drainage fluxes were calculated for the O, A, B and C horizon using the simple mass balance method, which is originally based on the assumption of conservation of mass between the input of atmospheric Cl^- and the Cl^- flux in the subsoil (Eriksson and Khunakasem, 1969). Because the conservative behaviour of Cl^- is subject to discussion (Svensson et al., 2012), we used sodium (Na^+) as a tracer instead of Cl^- as previously done by De Schrijver et al. (2004) and De Schrijver et al. (2008). The mass balance method requires the assumption of conservative behaviour of Na^+ in the soils. For the five Level II plots studied, we assumed that the contribution of weathering to Na^+ concentrations in the soil solution is negligible over the study period, given the minor amounts of Na-Feldspar and mica in the finer soil textures and the absence of these minerals in the sandy soils (Van Ranst et al., 2002). Also the amount of exchangeable Na^+ in the soils is very low (Mikkelsen et al., 2008). We furthermore assumed that the adsorption of Na^+ to clay mineral surfaces is negligible, given the very low soil pH-$CaCl_2$ (Table 2.2). As shown by a single chemical analysis in 2007 the amount of Na^+ taken up by ground vegetation is limited to 0.003–0.041 kg ha^{-1} and thus negligible (INBO, unpublished results). The same accounts for the amount of Na^+ taken up by the trees, since Na^+ concentrations in wood samples taken from stem discs at 1 m height were mostly below the LOQ of 50 mg kg^{-1} (INBO, unpublished results).

3   IMPACT OF DECLINING ATMOSPHERIC DEPOSITION ON FOREST SOIL SOLUTION CHEMISTRY IN FLANDERS, BELGIUM

Abstract

Throughout Europe and the USA, forest ecosystem functioning has been impacted by long-term excessive deposition of acidifying compounds. In this study, we report on trends in stand deposition and soil solution fluxes of inorganic nitrogen (N) and sulphur (S) compounds over a 17-year period (1994–2010) in five ICP Forests monitoring plots in Flanders, northern Belgium. Deposition was dominated by N, and primarily NH_4^+. Deposition of SO_4^{2-} and NH_4^+ declined by 56–68% and 40–59% respectively. Deposition of NO_3^- decreased by 17–30% in deciduous forest plots, but remained stable in coniferous forest plots. The decrease in N and S deposition was paralleled by a simultaneous decline in base cation (BC = Ca^{2+} + K^+ + Mg^{2+}) deposition, resulting in a 45–74% decrease in potentially acidifying deposition. Trends in soil solution fluxes of NH_4^+, NO_3^-, SO_4^{2-} and BC mirrored declining depositions. Nitrate losses below the rooting zone were eminent in both coniferous forest plots and in one deciduous forest plot, while net SO_4^{2-} release was observed in two deciduous forest plots. Critical limits for BC:Al_{tot} ratio were exceeded at the three plots on sandy soils with lower cation exchange capacity and base saturation. Soil solution acid neutralizing capacity increased but remained negative, indicating that soil solution acidification continued, as the start of recovery was

delayed by a simultaneous decrease in BC depositions and short-term soil buffering processes. Despite substantial reductions, current N deposition levels still exceed 4–8 times the critical load for safeguarding sensitive lichen species, and are still 22–69% above the critical load for maintaining ground vegetation diversity.

3.1   **Introduction**

Since the late 1970s atmospheric deposition of sulphur (S) and nitrogen (N) has been related to adverse effects on forest soil condition and soil solution chemistry throughout Europe and the USA (Ulrich et al., 1979; Aber et al., 1989; Alewell et al., 2000; MacDonald et al., 2002; Driscoll et al., 2003a; Monteith et al., 2007). According to these studies, soil acidification entailed elevated aluminium (Al) concentrations in soil solution, depletion of base cations from the soil exchange complex, diminished leaching of dissolved organic carbon following decelerated litter decomposition, and N saturation indicated by losses of NO_3^- below the rooting zone.

As soon as harmful effects of transboundary air pollution were recognized, abatement strategies were outlined within the Convention on Long-Range Transboundary Air Pollution (CLRTAP) of the United Nations Economic Commission for Europe (UNECE) (www.unece.org). The implementation of the so-called S protocols (Helsinki 1985, Oslo 1994) and the Gothenburg multi-pollutant protocol (1999) resulted in a reduction of SO_2 emissions in Western Europe by a factor 8–9 between 1980 and 2010, whereas emissions of nitrogen oxides (NO_x) and ammonia (NH_3) were reduced by 40% and 36% respectively (Granier et al., 2011; European Environment Agency, 2014). In Flanders, northern Belgium, emissions and depositions of potentially acidifying N and S compounds were reduced between 1990 and 2010 with respectively 61% (VMM, 2011) and 51% (VMM, 2012). Despite these reductions, current NO_x emissions in Flanders still exceed the 2010 ceilings set by European legislation (EU, 2001).

Several studies highlighted the unfavourable condition of forest soils in Belgium as a result of long-term excessive N and S depositions. A European study on ICP forests monitoring sites in several countries, including Belgium, revealed that critical limits for N concentrations in soil solution were frequently exceeded between the early 1990s and 2006 (Iost et al., 2012). Two coniferous forest plots in Flanders showed a steady decline of soil solution acid neutralizing capacity (ANC) and of molar Ca^{2+}/Al ratio between 1992 and 1997, despite decreasing depositions (Neirynck et al., 2002). Over a longer period, a

significant acidification of the upper layer (0.3–0.4 m) of several forest soil types was observed between 1950 en 1985 (Ronse et al., 1988). A follow-up study showed an ensued acidification of the mineral topsoil from podzols between 1985 and 2000 (De Schrijver et al., 2006).

Long-term monitoring of acidifying depositions and soil solution concentrations provides a valuable tool to evaluate abatement strategies and to track possible chemical recovery from long-term inputs. Data for stand deposition and soil solution chemistry in five ICP Forests intensive monitoring plots (Level II) are collected since 1994. Long-term records were analysed in order to: 1) evaluate trends in potentially acidifying depositions between 1994 and 2010, 2) investigate the effects of potentially acidifying depositions on soil solution chemistry, and 3) discuss the observed trends in relation to critical loads and levels. We hypothesized that potentially acidifying depositions decreased in Flemish forests during the study period and that this lowered the elemental concentrations in soil solution, leading to a better condition with regard to critical loads and levels.

3.2   **Materials and methods**

3.2.1   Study area

Five plots of the ICP Forests intensive monitoring network (Level II) in Flanders, northern Belgium, were included in this study. More details about these Level II plots are given in section 2.1.

3.2.2   Sample collection and measurements

Sampling of throughfall, stemflow and soil solution was carried out fortnightly from January 1994 till December 2010. A detailed description of the methods used for deposition sampling is given in section 2.2.1 and for soil solution sampling in section 2.2.2.

3.2.3   Chemical analysis

A description of the methods used for sample pre-treatment and for the determination of the concentrations (mg L^{-1}) of H^+, Al_{tot}, Ca^{2+}, K^+, Mg^{2+}, NH_4^+, Na^+, SO_4^{2-}, Cl^- and NO_3^- on the collected samples of throughfall, stemflow and soil solution is given in section 2.3.1.

3.2.4 Data handling

All field data (e.g. sample weights) and analytical results were subjected to a detailed quality check and validation procedure, according to the guidelines of the ICP Forests Working Group on Quality Assurance/Quality Control (Mosello et al., 2005). Throughfall and stemflow data showed only minor irregularities and validated data from all years were included in the data analysis. Soil solution data showed some inconsistencies and missing values as a result of drought periods and consequently low sampling volumes, especially during the first years after installation. These data were excluded from further analysis, reducing the time span of several data series.

Stand deposition was calculated as the sum of throughfall and stemflow deposition (further denoted as TF). Taking TF as a variable instead of total deposition means that we did not correct for canopy exchange (canopy uptake of NH_4^+, H^+ and NO_3^-, canopy leaching of Ca^{2+}, K^+, Mg^{2+}, Na^+, Cl^-, SO_4^{2-} and weak acids, ...). This way the many uncertainties and assumptions associated with the use of canopy budget models (Staelens et al., 2008; Adriaenssens et al., 2013) were avoided. Moreover, as TF represents the amount of deposition that reached the forest floor, and as such directly affects soil solution chemistry, it is more relevant in the context of this study than total deposition. Stand deposition was corrected for inputs from marine sources (Stedman et al., 1990). Deposition of potentially acidifying compounds (ACID) was calculated as the sum of NO_3^-, NH_4^+, SO_4^{2-} and Cl^-, corrected for the neutralizing effect of BC (BC = Ca^{2+} + K^+ + Mg^{2+}), according to UNECE (2004).

Drainage fluxes were calculated for the O, A, B and C horizon using the mass balance method (see section 2.4). Annual soil fluxes of individual elements were then calculated by multiplying the drainage flux with mean annual soil solution concentrations at each depth. We assumed that elemental fluxes through the C horizon represented losses below the rooting zone. The ANC was obtained by subtracting the sum of SO_4^{2-}, NO_3^- and Cl^- from the sum of BC and Na^+ in mol_c. It was multiplied by the precipitation surplus to allow comparison with deposition fluxes. The BC:Al_{tot} ratio for the mineral soil solution was calculated as the ratio of the sum of BC to Al_{tot} in mol_c, assuming that Al ions were entirely present as Al^{3+}.

3.2.5   Statistical analysis

Data exploration and statistical analysis were performed in S-plus for Windows, version 6.2. The nonparametric Seasonal Mann-Kendall Test (Hirsch et al., 1982) was applied to detect monotonic trends in three-monthly aggregated data representing the four seasons (January-March, ..., September-December) for TF and soil solution fluxes. This test allows to detect possible effects of seasonality, unlike classical linear regression. Trends were evaluated by the significance of Theil-Sen's slope, which is the median change between years for all seasonal blocks (Sen, 1968). In order to ascertain whether SO_4^{2-}, NH_4^+ and NO_3^- were retained within the ecosystem, their mean annual output/input ratio was calculated for each soil depth. Differences between input (TF) and output (soil solution fluxes at each depth) were evaluated using a paired t-test. Cross-site statistics were performed by means of ANOVA/Tukey's range test. We used two critical limits to evaluate whether soils showed chemical recovery and were protected against aluminium toxicity: ANC = 0 (Holmberg et al., 2001) and BC:Al$_{tot}$ ratio (BC:Al$_{tot}$ = 1.2 for *Pinus*; BC:Al$_{tot}$ = 0.6 for *Quercus* and *Fagus*) (Sverdrup and Warfvinge, 1993; UNECE, 2004).

3.3   **Results**

3.3.1   Trends in potentially acidifying depositions

Depositions of non-marine SO_4^{2-} and NH_4^+ significantly declined at all plots by 56–68% and 40–59% respectively (Table 3.1, Figure 3.1). Depositions of NO_3^- decreased significantly in deciduous forest plots by 17–30%, but remained stable in coniferous forest plots. However, NO_3^- depositions decreased only during the first two years (1994–1996) and were stable thereafter. Depositions of N and S were highest in coniferous forest plots. Molar NH_4^+:NO_3^- ratios declined significantly at all locations from 2.44 to 1.90 (plot-averaged ratio). Depositions of BC decreased significantly at all plots by 19–41% and were highest in deciduous forest plots. Depositions of ACID decreased significantly at all plots by 45–74% and were highest in coniferous forest plots. We did not observe any relation between tree species or site and the rate of decrease in ACID depositions.

Table 3.1 Seasonal Mann-Kendall trends (1994–2010) for TF (sea salt corrected) with mean value in mm yr^{-1} (stand precipitation) or mol$_c$ ha^{-1} yr^{-1} (NH_4^+, NO_3^-, SO_4^{2-}, BC, ACID), mean molar ratio (NH_4^+:NO_3^-), letters (a-d) indicating groups of plots with comparable mean (p < 0.05) and Theil-Sen's slope with significance (ns: not significant, *: p < 0.05, **: p < 0.01, ***: p < 0.001).

| Plot	Stand		NH_4^+		NO_3^-		NH_4^+:NO_3^- (molar)		SO_4^{2-}		BC		ACID	
	Mean (mm yr^{-1})	Slope	Mean (mol$_c$ ha^{-1} yr^{-1})	Slope	Mean (mol$_c$ ha^{-1} yr^{-1})	Slope	Mean (-)	Slope	Mean (mol$_c$ ha^{-1} yr^{-1})	Slope	Mean (mol$_c$ ha^{-1} yr^{-1})	Slope	Mean (mol$_c$ ha^{-1} yr^{-1})	Slope
RAV	636a	ns	1901d	-69***	645b	ns	2.96c	-0.09***	1229bc	-63***	733a	-11*	2995d	-127***
BRA	784b	ns	1576c	-49***	709b	ns	2.24b	-0.05***	1380c	-70***	966b	-25***	2593c	-93***
WIJ	712ab	ns	1370bc	-72***	519a	-7*	2.67bc	-0.09***	1021ab	-59***	1209bc	-19*	1763b	-120***
GON	657a	ns	1155b	-49***	529a	-9*	2.18b	-0.06***	1212bc	-62***	1741d	-23**	1198a	-84***
HOE	743b	ns	806a	-42***	521a	-12***	1.53a	-0.05***	869a	-53***	1400c	-47***	816a	-56***
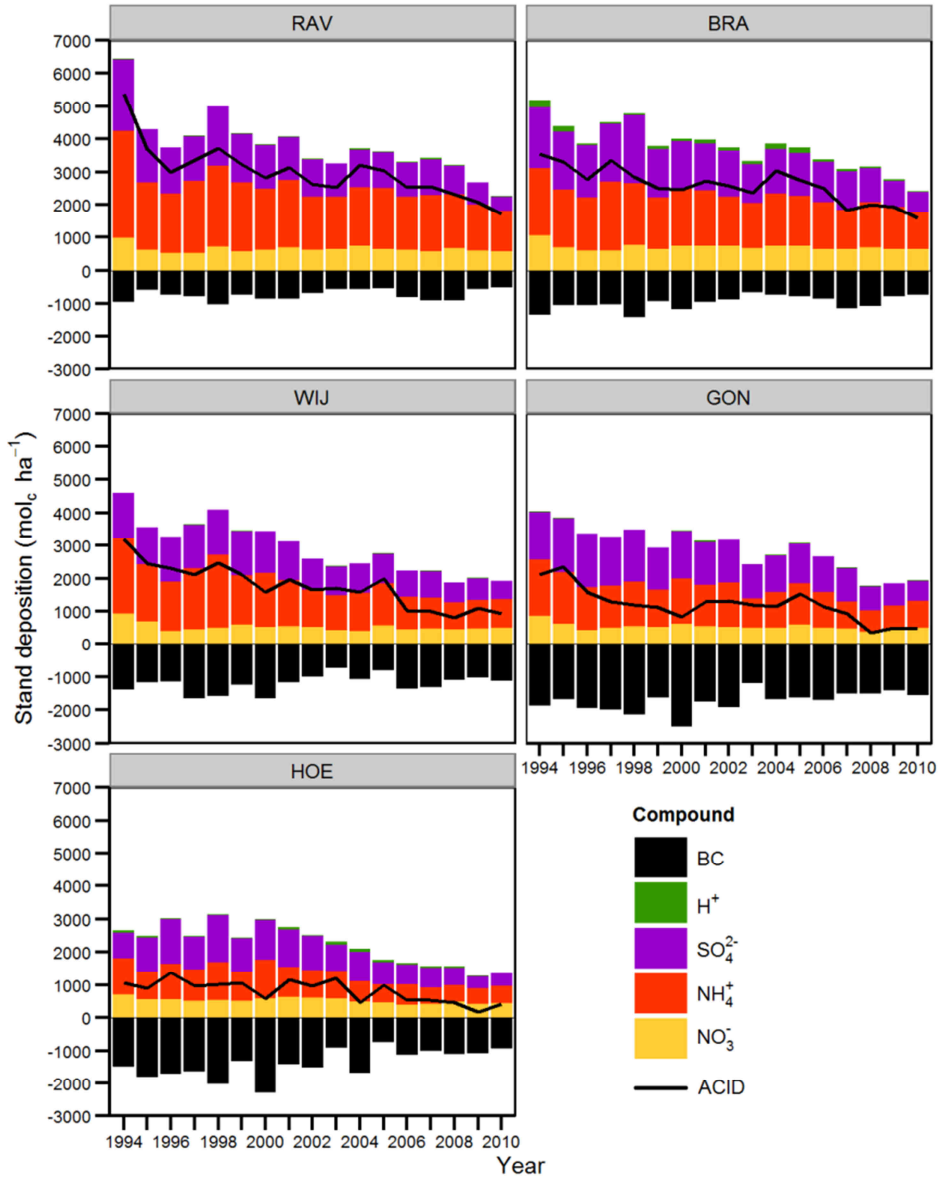
Figure 3.1 Annual TF (sea salt corrected) in mol_c ha^{-1} of BC (multiplied by -1), H^+, SO_4^{2-}, NH_4^+, NO_3^- and ACID.

3.3.2   Trends in soil solution fluxes

Soil solution fluxes of SO_4^{2-} decreased significantly at most depths in all plots (Table 3.2, Figure 3.2). Fluxes of NH_4^+ through the O horizon decreased significantly in BRA, but remained stable at the other plots. In the mineral soil, fluxes of NH_4^+ were negligible. Soil solution fluxes of NO_3^- in coniferous forest plots decreased significantly in the mineral soil, but remained stable in the O horizon. In two deciduous forest plots (WIJ, HOE) fluxes of NO_3^- declined throughout the entire soil profile, but in GON this was confined to the C horizon. In the O horizon, NO_3^- fluxes were lower in coniferous than deciduous forest plots. In the mineral soil, on the contrary, the lowest NO_3^- fluxes were observed in two deciduous forest plots (WIJ, HOE), while strongly elevated NO_3^- fluxes were found in GON. The decrease in the soil solution fluxes of SO_4^{2-} and NO_3^- was accompanied by a decrease in BC and Al. Aluminium prevailed in the soil chemistry of the more sandy soils (RAV, BRA, WIJ), where the buffer system from the whole soil profile had entered the Al buffer range. Soil solution ANC increased significantly in three plots (BRA, WIJ, HOE), and remained nearly stable in the other plots (Figure 3.3). Mean ANC was below 0 except in the O horizon in HOE. In the mineral soil, BC:Al$_{tot}$ ratios decreased in three plots (RAV, WIJ, HOE) and remained nearly stable in the other plots (Figure 3.4). Critical limits for BC:Al$_{tot}$ ratio were never exceeded in two deciduous forest plots (GON, HOE), but were permanently exceeded in the coniferous forest plots and in the B and C horizon of one deciduous forest plot (WIJ).

Table 3.2 Seasonal Mann-Kendall trends for soil solution fluxes with the examined period in years, mean value in mm yr^{-1} (precipitation surplus) or mol$_c$ ha^{-1} yr^{-1} (SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, BC, Al$_{tot}$, H$^+$, ANC), mean molar ratio (BC:Al$_{tot}$), letters (a-d) indicating groups of plots with comparable mean (p < 0.05) and Theil-Sen's slope with significance (ns: not significant, *: p < 0.05, **: p < 0.01, ***: p < 0.001).

Plot	Period	Sampling Depth (cm)	Prec. surplus Mean (mm yr^{-1})	Slope	SO$_4^{2-}$ Mean (mol$_c$ ha^{-1} yr^{-1})	Slope	NH$_4^+$ Mean (mol$_c$ ha^{-1} yr^{-1})	Slope	NO$_3^-$ Mean (mol$_c$ ha^{-1} yr^{-1})	Slope	BC Mean (mol$_c$ ha^{-1} yr^{-1})	Slope
O horizon												
RAV	1994-2010		476a	ns	997ab	-36***	709a	ns	1113ab	ns	1477a	ns
BRA	1994-2010		560ab	ns	1383c	-64***	722ab	-64***	791a	ns	1440a	ns
WIJ	2003-2010		662b	ns	861a	-53**	379c	ns	2590c	-192*	2979b	ns
GON	1994-2010		469a	ns	1268bc	-26*	495bc	ns	1852d	ns	3244b	ns
HOE	1994-2010		508a	ns	881a	-21*	352c	ns	1373b	-30*	2806b	ns
A horizon												
RAV	1997-2010	10-25	353ab	ns	1111a	-67***	88a	ns	1631b	-89**	887a	-80***
BRA	2002-2010	15-25	319ab	ns	1127ab	-47*	10a	ns	949a	ns	720a	-52*
WIJ	2002-2010	10-20	351ab	ns	914a	-61**	7a	ns	756a	-160***	828a	ns
GON	1996-2010	10-20	317a	ns	1492b	-77***	30a	+1**	2302c	ns	3017b	-89***
HOE	2001-2010	10-15	418b	-21*	779a	-74***	6a	ns	676a	-104***	1198a	-205***
B horizon												
RAV	2002-2010	30-45	267a	ns	874a	ns	10a	ns	1291ac	-141**	372a	-34**
BRA	1994-2010	30-55	280a	ns	1487b	-76***	132b	-1**	1570bc	-130***	953b	-61***
WIJ	1998-2010	45-70	250a	ns	1105a	-59***	9a	ns	1098ab	-167***	788ab	-105***
GON	1999-2010	25-40	326ab	ns	1198ab	ns	10a	+1***	1928c	ns	2310c	-94**
HOE	1998-2010	20-30	415b	-18**	954a	-62***	33a	ns	615a	-44***	1202b	-144***
C horizon												
RAV	1994-2010	70-95	221ab	+14***	1353ab	ns	4a	ns	1365b	-51*	480a	-29***
BRA	1997-2010	70-90	300bc	-12***	1683b	-82***	3a	ns	1120b	-104***	738a	-68***
WIJ	2002-2010	75-110	197a	-8*	1178a	-69**	1a	-0.2*	351a	-64***	466a	-47***
GON	1994-2010	45-55	255ab	-9**	1389ab	-71***	6a	ns	1321b	-84***	2009c	-104***
HOE	1996-2010	35-55	377c	ns	1091a	-60***	3a	ns	504a	-28***	1225b	-89***

Table 3.2 continued.

Plot	Period	Sampling Depth (cm)	Al$_{tot}$ Mean (mol$_c$ ha^{-1} yr^{-1})	Al$_{tot}$ Slope	H$^+$ Mean (mol$_c$ ha^{-1} yr^{-1})	H$^+$ Slope	ANC Mean (mol$_c$ ha^{-1} yr^{-1})	ANC Slope	BC:Al$_{tot}$ (molar) Mean (-)	BC:Al$_{tot}$ Slope
O horizon										
RAV	1994-2010				336b	+26***	-1474a	ns		
BRA	1994-2010				405b	+41***	-1508a	+110***		
WIJ	2003-2010				732c	-93**	-1158ab	+189**		
GON	1994-2010				97a	+5**	-573b	ns		
HOE	1994-2010				38a	+4***	+113c	+43**		
A horizon										
RAV	1997-2010	10-25	1811b	ns	1155b	ns	-2020a	ns	0.49b	-0.04***
BRA	2002-2010	15-25	1006a	-135***	1101b	ns	-1548ab	+92*	0.84ab	+0.07*
WIJ	2002-2010	10-20	786a	-76**	1016b	-112***	-1105bc	+161***	1.05ab	-0.05*
GON	1996-2010	10-20	982a	-34*	527a	+44***	-901c	ns	3.15c	ns
HOE	2001-2010	10-15	590a	-46**	290a	-18*	-321d	+24*	1.99a	-0.19***
B horizon										
RAV	2002-2010	30-45	2615d	ns	330ab	ns	-1874a	+158**	0.14a	-0.01***
BRA	1994-2010	30-55	1398bc	-83***	986c	-50***	-2205a	+173***	0.71a	ns
WIJ	1998-2010	45-70	1872c	-140***	296ab	-20***	-1580a	+128***	0.37a	-0.03***
GON	1999-2010	25-40	961ab	ns	449b	ns	-902c	ns	2.45b	-0.10***
HOE	1998-2010	20-30	550a	ns	172a	-5*	-445c	ns	2.43b	-0.27***
C horizon										
RAV	1994-2010	70-95	2999d	ns	171ab	ns	-2465a	ns	0.15a	-0.01***
BRA	1997-2010	70-90	2165c	-151***	488c	-28***	-2126a	+133***	0.35a	-0.02***
WIJ	2002-2010	75-110	1395b	-118***	138ab	ns	-1319b	+115***	0.33a	-0.01**
GON	1994-2010	45-55	899ab	-67***	254b	-11***	-821bc	ns	2.33b	+0.05**
HOE	1996-2010	35-55	492a	-15*	116a	ns	-433c	+18*	2.52b	-0.11**

a) O horizon

Coniferous stands
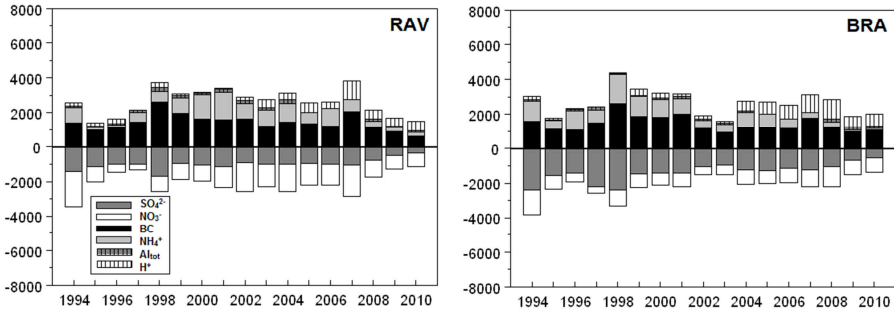
Deciduous stands
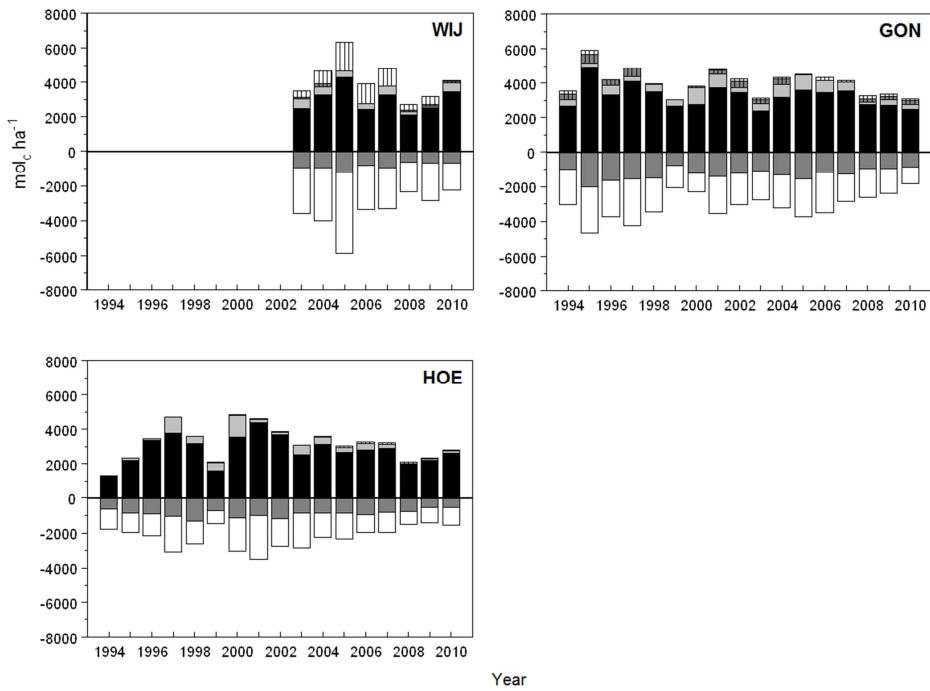
Figure 3.2 Annual soil solution flux in mol_c ha^{-1} for H^+, Al_{tot}, BC, NH_4^+, SO_4^{2-} and NO_3^- in the O horizon (a), A horizon (b), B horizon (c) and C horizon (d). Values for SO_4^{2-} and NO_3^- were multiplied by (-1) to illustrate the charge balance (anions vs. cations).

b) A horizon

Coniferous stands
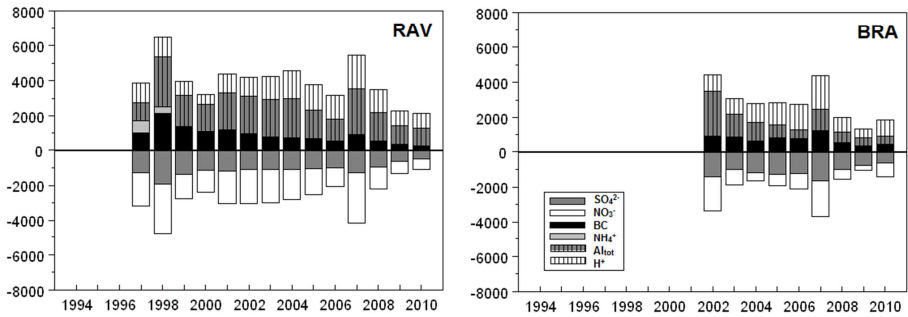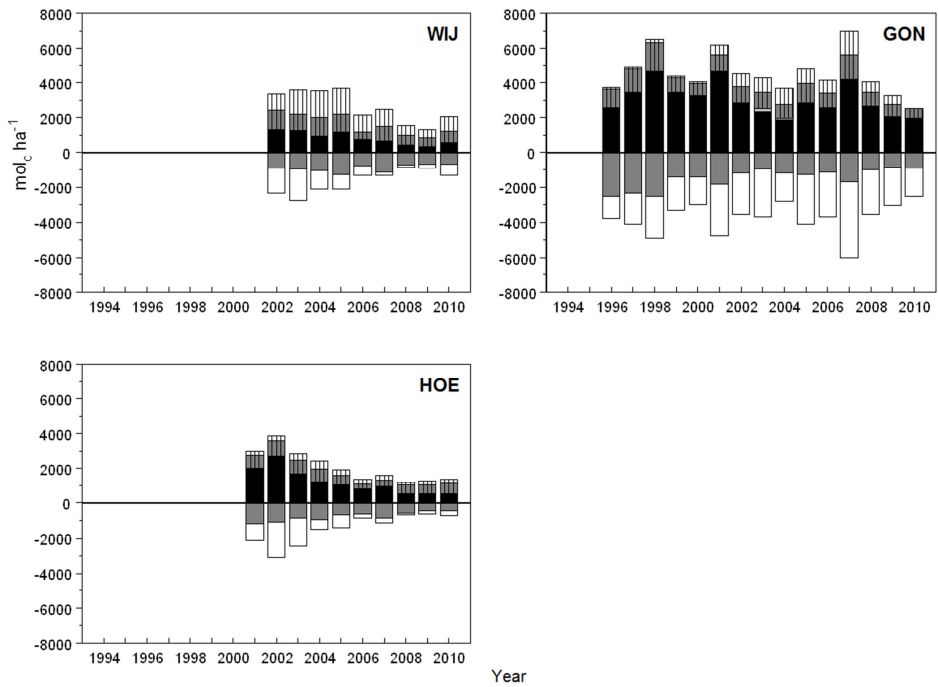
Deciduous stands

Figure 3.2 continued.

c) B horizon

<u>Coniferous stands</u>
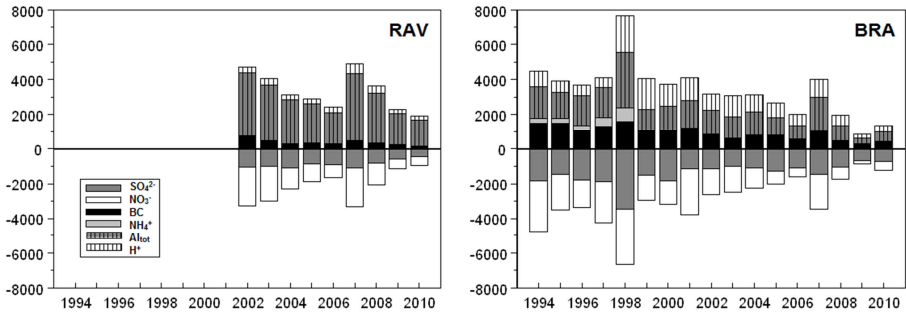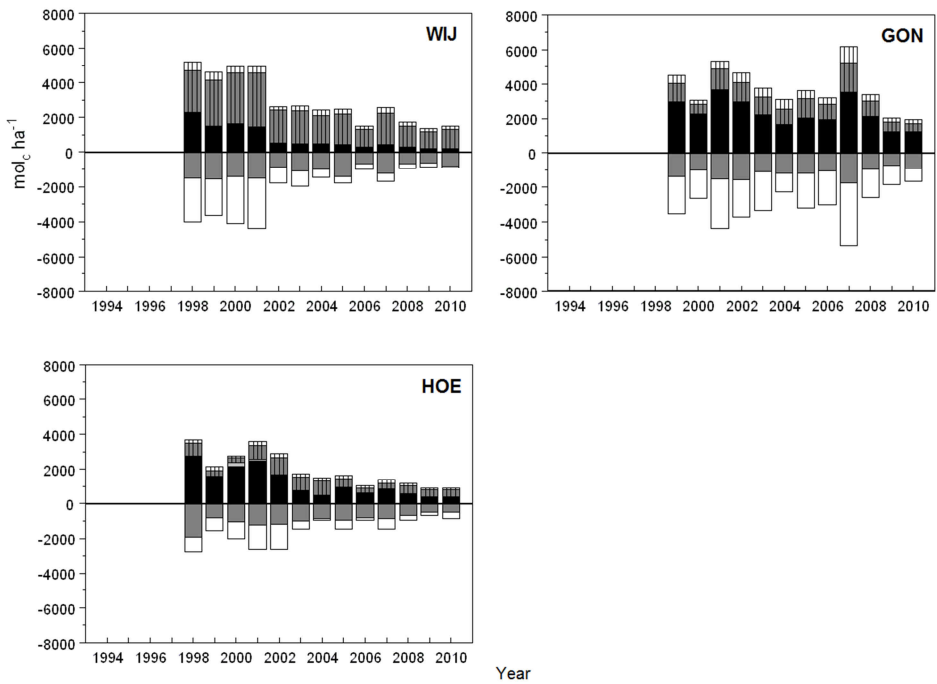
<u>Deciduous stands</u>

Figure 3.2 continued.

d) C horizon

Coniferous stands

Deciduous stands

Figure 3.2 continued.

Coniferous stands
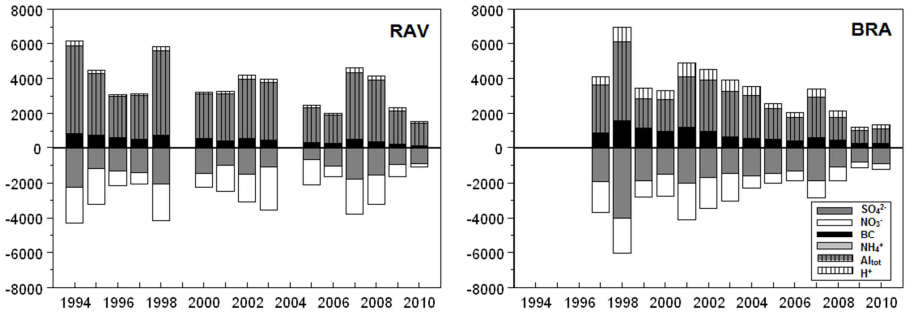
Deciduous stands
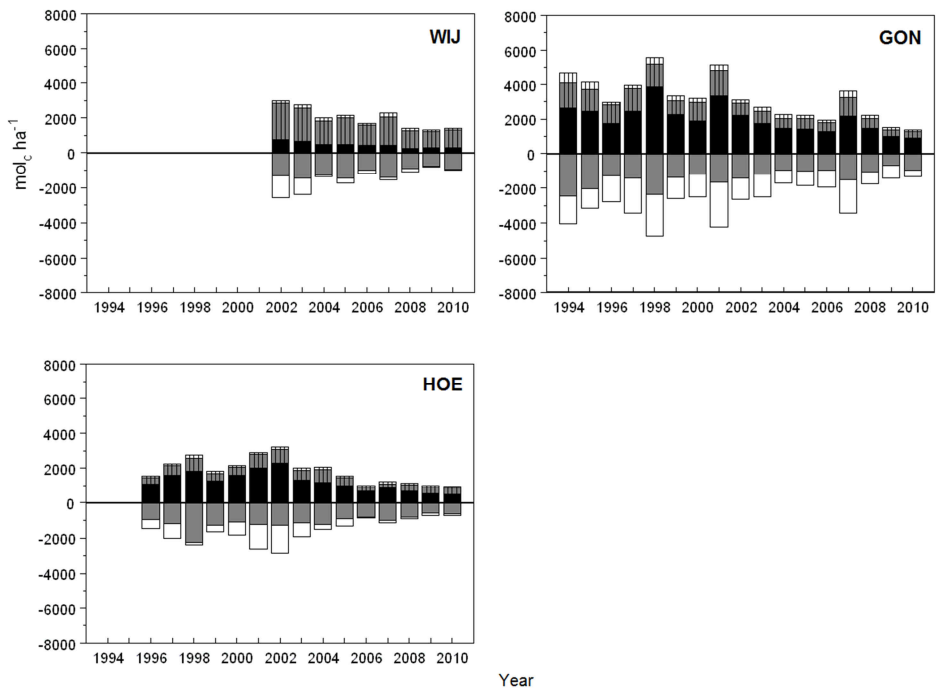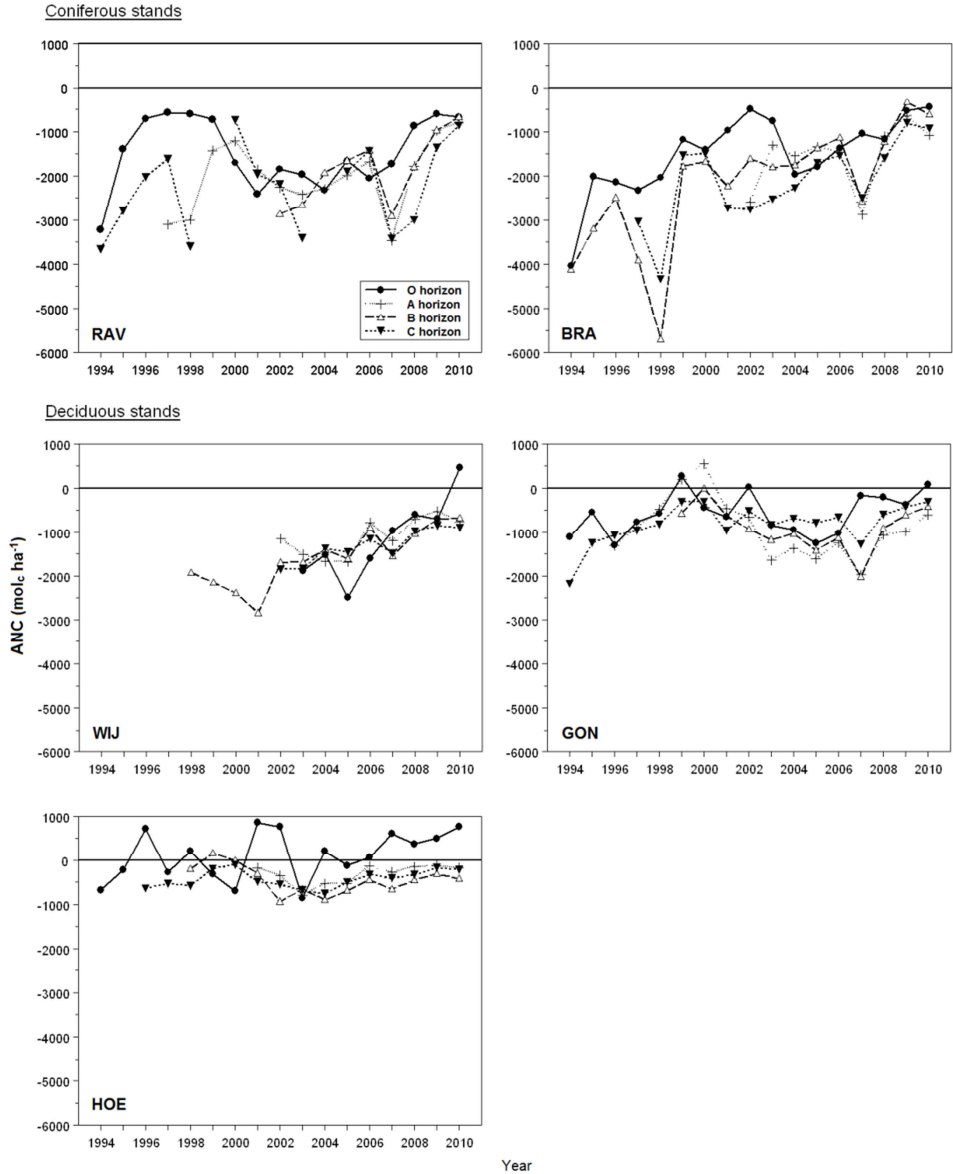
Figure 3.3 Annual average ANC values (multiplied by precipitation surplus) in mol_c ha^{-1} for each soil depth. Positive values indicate recovery, negative values a proceeding of soil solution acidification.

Coniferous stands

Deciduous stands
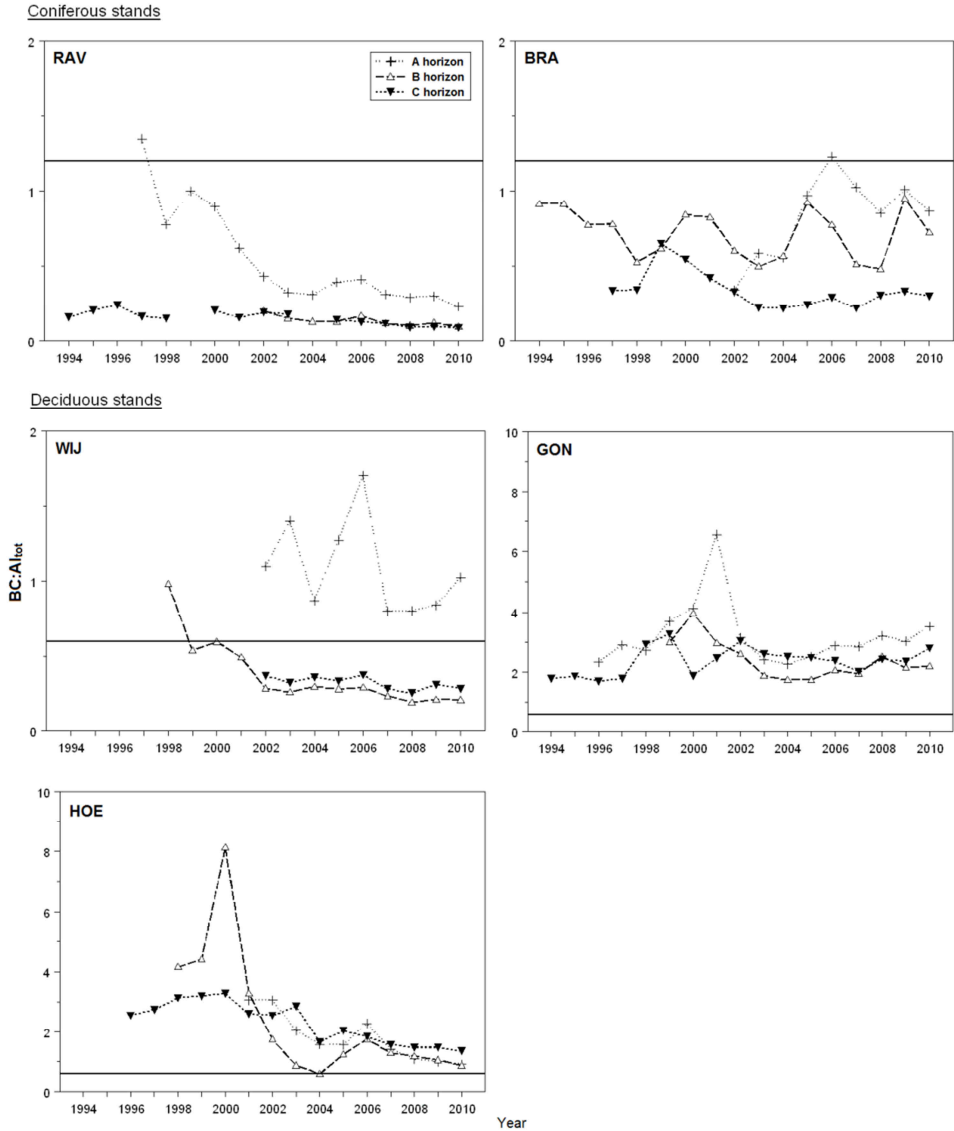
Figure 3.4 Annual median BC:Al$_{tot}$ ratios for the mineral soil. Horizontal lines indicate critical limits (Sverdrup and Warfvinge, 1993; UNECE, 2004) for damage to fine roots, reduced tree stability, inhibited root growth and growth reductions of up to 80% of mean growth for beech/oak (0.6) and pine (1.2).

3.3.3   Ion budgets of SO_4^{2-}, NO_3^- and NH_4^+

Coniferous forest plots showed significant retention of SO_4^{2-} in the upper soil layers, but outputs were not different from inputs in the C horizon (Table 3.3). In the deciduous forest plots, outputs of SO_4^{2-} were not different from inputs in the upper soil layers, but outputs of SO_4^{2-} were significantly higher than inputs in the C horizon at two plots (WIJ, HOE). The degree of inorganic N leaching showed considerable differences among the plots. In the O horizon, retention of N was observed in coniferous forest plots, while deciduous forest plots showed significant net losses of N. One deciduous forest plot (GON) also showed significant net losses of N from the A horizon. Losses of N below the rooting zone varied from 16% (WIJ) to 76% (GON) of inorganic N inputs.

Table 3.3 Ion budget for TF (inputs) and soil solution fluxes (outputs) expressed as % (outputs/inputs*100) for SO_4^{2-} (including inputs from sea salt) and $NH_4^+ + NO_3^-$ for the different soil depths. Between brackets the mean annual difference between inputs and outputs (mol_c ha^{-1} yr^{-1}) is shown when significant (*: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$).

Plot	Period	O horizon SO_4^{2-}	$NH_4^+ + NO_3^-$	A horizon SO_4^{2-}	$NH_4^+ + NO_3^-$	B horizon SO_4^{2-}	$NH_4^+ + NO_3^-$	C horizon SO_4^{2-}	$NH_4^+ + NO_3^-$
RAV	2002–2010	80(198***)	84	93(75*)	67(727**)	84(165***)	57(943**)	124	58(882**)
BRA	2002–2010	82(231***)	60(827***)	89	47(1103**)	84(207**)	48(1076***)	108	41(1214***)
WIJ	2003–2010	96	199(1505**)	101	45(784**)	104	27(1066***)	129(263**)	16(1220***)
GON	1999–2010	101	146(672***)	108	168(924**)	104	129	102	76(376*)
HOE	2001–2010	112	142(509**)	100	54(454*)	112(76*)	46(573***)	127(179***)	37(640***)

3.4   **Discussion**

3.4.1   Trends in potentially acidifying deposition

Depositions of inorganic N and SO_4^{2-} in Flanders range within the highest deposition classes defined for European Level II plots (Lorenz et al., 2008). This could be explained by the abundance of emission sources in this part of Europe, which is a densely populated, industrialized region, characterized by an important animal husbandry sector, and an intensively used road network. The observed deposition levels and decreasing trends of SO_4^{2-}, NH_4^+ and NO_3^- are comparable to results reported for Level II plots in neighbouring regions like southern Belgium (Jonard et al., 2012), northern France (van der Heijden et al., 2011) and southern UK (Vanguelova et al., 2010). Our hypothesis that depositions decreased was thus generally withhold for SO_4^{2-}, NH_4^+ but only at three out of five locations for NO_3^- (and rejected for NO_3^- if the first two years are disregarded).

The strong decline of non-marine SO_4^{2-} depositions can be attributed to the measures taken by industry and power plants to reduce SO_2 emissions, which had already dropped below 1880 levels in 2010 (Mylona, 1996; VMM, 2011). The decrease in NH_4^+ can be attributed to NH_3 emission reductions by the agricultural sector (EEC, 1991) and a declining co-deposition with SO_4^{2-} (Cape et al., 1998). Depositions of NO_3^- diminished to a much lower extent or even remained stable. Traffic is responsible for 52–60% (1990–2010) of NO_x emissions in Flanders (VMM, 2011) and the highest NO_y depositions were observed near intensively used highways connecting the cities of Brussels, Antwerp and Ghent (MIRA, 2006). It appears that the effect of introducing low-emission vehicles in agreement with EU emission standards was counteracted by the increasing traffic density and the growing number of diesel vehicles.

3.4.2   Effects on soil solution chemistry

We observed that soil SO_4^{2-} fluxes decreased significantly in all plots, which confirmed our hypothesis, but to a lesser degree than we could expect from the observed decrease in S deposition, and we found a net release of SO_4^{2-} at two deciduous forest plots. Net release of SO_4^{2-} following a decline in SO_4^{2-} depositions has been reported in several European catchments (Prechtel et al., 2001), and may delay the de-acidification process by simultaneous release of H^+ (Karltun, 1997).

We found that fluxes of NO_3^- in the mineral soil decreased significantly at most soil depths in all plots, in reaction to declining inorganic N depositions, which confirmed our hypothesis. However, with an average leaching of 5–19 kg N ha^{-1} yr^{-1} over the study period, the limit of 2–3 kg N ha^{-1} yr^{-1} for elevated NO_3^- leaching was exceeded at all plots (Gundersen et al., 2006). Differences in NO_3^- leaching between the five plots could be explained by a combination of factors, like the local pollution climate (see section 2.1), tree species (in general, higher N uptake in deciduous species (Gundersen et al., 2009), soil C/N ratio related to litter quality and microbial activity (in general, higher leaching when C/N ratio decreases (MacDonald et al., 2002), site fertility (Kristensen et al., 2004) and by consequence also site history (in general, higher degree of NO_3^- leaching in post-agricultural forests due to application of fertilizer (Callesen et al., 1999). In our study the role of site history is unclear, as the highest NO_3^- losses were observed at one of the old growth forest plots and the lowest at the plot on former arable land. The excessive losses of NO_3^- below the rooting zone in one deciduous forest plot (GON) are probably the result of more intense internal N processes, like humus disintegration mediated by drought periods (Eichhorn and Hüttermann, 1999).

We want to remark that it would be useful to calculate soil water fluxes based on detailed water balance models as described in the ICP Forests manual, Part XI (Nieminen et al., 2016) and compare the outcome with the results for the sodium mass balance.

3.4.3   Critical loads and levels

As one of the species groups most sensitive to elevated air concentrations and depositions of N and S, epiphytic lichens and mosses serve as good bio-indicators for air pollution (Conti and Cecchetti, 2001). Based on empirical research on lichens in forests, a critical load of 221 mol_c N ha^{-1} yr^{-1} was deduced for TF (Fenn et al., 2008). In our study, TF of inorganic nitrogen in 2010 varied between 977 and 1806 mol_c N ha^{-1} yr^{-1} at the five plots, which is 4 to 8 times higher than the critical load for sensitive lichen populations.

For ground vegetation in temperate forests, an empirical critical load range of 714–1071 mol_c N ha^{-1} yr^{-1} was deduced (Fenn et al., 2008). Above this level species diversity of ground vegetation may decrease by disappearance of species adapted to conditions of low nutrient availability. In 2010, the upper limit of this critical load for ground vegetation was respected in only one plot (HOE) and was still exceeded by 22–69% in the other four

plots. Our hypothesis that the decrease in depositions resulted in a better condition with regard to critical loads was thus rejected.

Iost et al. (2012) demonstrated that the critical limits for N concentrations in soil solution are largely exceeded during most part of the year at all depths at the five plots. We observed that the critical limit for the BC:Al$_{tot}$ ratio was exceeded continuously over the past 17 years in the coniferous forest plots and in the B and C horizon of one deciduous forest plot (WIJ). In these plots trees may suffer more from root damage, which could lead to significant growth reductions. Two deciduous forest plots where the critical limit for BC:Al$_{tot}$ was respected (GON, HOE), receive lower ACID depositions and have soils with higher base saturation and cation exchange capacity, which may explain the difference with the other plots.

We observed that ANC of soil solution remained < 0, except in the O horizon of one plot (HOE). This means that the acidification of forest soil solution in Flanders continued, despite a significant reduction of ACID depositions. The steady continuation of soil solution acidification, although at a slower pace compared to the start of the monitoring campaign, can be ascribed to a great extent to the simultaneous decrease in BC depositions and its impact on cation exchange processes (Alewell et al., 2000). Also, other soil buffering processes like SO_4^{2-} desorption (see section 3.4.2), which are not well studied, further delay the start of recovery. Our hypothesis that the decrease in depositions resulted in a better condition with regard to critical limits was thus only partially supported.

3.5 Conclusions

Potentially acidifying N and S depositions on Flemish forests decreased significantly between 1994 and 2010, but forest soils in Flanders are still in an unfavourable condition. Critical loads and levels were still exceeded and soil solution acidification due to human disturbances continued, because a simultaneous decline of BC depositions and short-term soil buffering processes like SO_4^{2-} desorption delay recovery.

4   IMPACT OF AIR-BORNE OR CANOPY-DERIVED DISSOLVED ORGANIC CARBON (DOC) ON FOREST SOIL SOLUTION DOC IN FLANDERS, BELGIUM

Abstract

Dissolved organic carbon (DOC) in the soil solution of forests originates from a number of biologically and/or biochemically mediated processes, including litter decomposition and leaching, soil organic matter mineralization, root exudation, mucilage and microbial activity. A variable amount of DOC reaches the forest floor through deposition, but limited information is available about its impact on soil solution DOC. In this study, trends and patterns of soil solution DOC were evaluated in relation to deposition of DOC over an 11-year period (2002–2012) at five ICP Forests intensive monitoring plots in Flanders, northern Belgium. Trend analysis over this period showed an increase in soil solution DOC concentrations for all observed depth intervals. Fluxes of DOC increased in the O horizon, but were nearly stable in the mineral soil. Annual leaching losses of DOC were higher in coniferous (55–61 kg C ha^{-1}) compared to deciduous plots (19–30 kg C ha^{-1}) but embody less than 0.05% of total 1-m soil organic C stocks. Temporal deposition patterns could not explain the increasing trends of soil solution DOC concentrations. Deposition fluxes of DOC were strongly correlated with soil solution fluxes of DOC, but their seasonal peaks were not simultaneous, which confirmed that air-borne or canopy-derived DOC has a limited impact on soil solution DOC.

4.1 **Introduction**

Dissolved organic carbon (DOC) plays an important role in the C cycle in forest ecosystems and contributes to the sequestration of C in mineral soils (e.g. Neff and Asner, 2001; Buurman and Jongmans, 2005). It is a highly dynamic soil organic C pool and facilitates the transport and/or bioavailability of nutrients and pollutants, such as nitrogen (N), phosphorus, sulphur and trace metals (Qualls et al., 1991; Kalbitz et al., 2000). It also forms a major pathway for C transfer from terrestrial to aquatic ecosystems, and provides a significant indirect source of CO_2 emission to the atmosphere (Freeman et al., 2001; 2004; Cole et al., 2007).

During the past decennia DOC concentrations and/or fluxes increased in many forests, peatlands, streams and lakes of northern and central Europe and eastern North America, while stable or decreasing DOC trends in these areas were less frequently observed (Freeman et al., 2001; 2004; Monteith et al., 2007; Lindroos et al., 2008; Oulehle and Hruška, 2009; Wu et al., 2010a; Löfgren and Zetterberg, 2011; Couture et al., 2012; Akselsson et al., 2013). Besides to climate change, rising DOC levels have been attributed to changes in soil solution chemistry induced by the overall decline of sulphur depositions, suggesting that ecosystems are recovering towards their high-DOC, pre-industrial state (de Wit et al., 2007; Oulehle and Hruška, 2009; Borken et al., 2011; Evans et al., 2012). A decline of acidifying depositions repeatedly leads to a decrease in soil solution ionic strength and pH increase, which both enhance DOC solubility in forest soils (Kalbitz et al., 2000; Vanguelova et al., 2010; Graf Pannatier et al., 2011; Evans et al., 2012; Kerr and Eimers, 2012; Verstraeten et al., 2012). The main source of DOC in the soil solution of forests are a number of biologically and/or biochemically mediated processes, including plant and root litter decomposition and leaching, soil organic matter mineralization, root exudation, mucilage and microbial activity (Kalbitz et al., 2000; Yano et al., 2000; Hansson et al., 2010). The main factors explaining soil solution DOC levels are tree species and soil type. Generally higher DOC levels are recorded in coniferous compared to deciduous forests, primarily due to more intensive leaching of DOC from an evergreen canopy, the higher C:N ratio of needles compared to leaves and the higher mass of the forest floor in coniferous forests (Currie and Aber, 1997; Borken et al., 2011; Arisci et al., 2012). Highly podzolized soils tend to have a lower DOC retention capacity than less acidified soils and may exhibit unusually high DOC outputs (Guggenberger and Zech, 1993).

Soil solution DOC levels display a characteristic seasonal pattern and a depth pattern in the soil profile. Peak concentrations are observed near the second half of the growing season in response to higher soil temperatures, while the highest C losses coincide with elevated water fluxes during the winter period (Buckingham et al., 2008; Sleutel et al., 2009; Wu et al., 2010a; Gielen et al., 2011). Concentrations and fluxes of DOC generally decrease with depth, due to translocation from the organic layer towards the mineral B horizon, where C is removed from soil solution mainly by abiotic processes, like precipitation as organo-metal complexes and/or by adsorption to solid Fe- and Al-phases (Guggenberger and Zech, 1993; Michalzik et al., 2001; Jansen et al., 2005; Fuss et al., 2011).

A considerable amount of DOC reaches the forest floor through atmospheric deposition or canopy leaching, but limited information is available about its role in the forest C cycle and its impact on soil solution DOC (Yano et al., 2000; Michalzik et al., 2001; Sleutel et al., 2009). In this study, we examined the contribution of air-borne or canopy derived DOC to concentrations and fluxes of soil solution DOC and their seasonal patterns using long-term monitoring data.

Long-term monitoring of deposition and soil solution concentrations provides valuable data to evaluate changes in soil solution chemistry. Flanders is participating in the ICP Forests programme (www.icp-forests.org), launched in 1985 under the Convention on Long-Range Transboundary Air Pollution (CLRTAP) of the United Nations Economic Commission for Europe (UNECE, www.unece.org). The objectives of this study are: 1) to evaluate trends and patterns of soil solution DOC concentrations and fluxes and 2) to assess the impact of air-borne or canopy-derived DOC on fluxes, concentrations and seasonal patterns of soil solution DOC. We hypothesized that soil solution DOC concentrations and fluxes increased during the study period and that this increase was strongly related to changes in air-borne or canopy-derived DOC.

4.2   **Materials and Methods**

4.2.1   Study area

Five plots of the ICP Forests intensive monitoring network (Level II) in Flanders, northern Belgium, were included in this study. More details about these Level II plots are given in section 2.1.

4.2.2   Sample collection and measurements

Sampling of throughfall, stemflow and soil solution was carried out fortnightly from January 2002 till December 2012. A detailed description of the methods used for deposition sampling is given in section 2.2.1 and for soil solution sampling in section 2.2.2.

4.2.3   Chemical analysis

A description of the methods used for sample pre-treatment and for the determination of DOC concentrations (mg L^{-1}) on the collected samples of throughfall, stemflow and soil solution is given in section 2.3.1.

4.2.4   Data handling

All field data (e.g. sample mass) and analytical results were subjected to a detailed quality check and validation procedure, according to the guidelines of the ICP Forests Working Group on Quality Assurance/Quality Control (König et al., 2016). Deposition of DOC (kg ha^{-1}) was calculated as the product of DOC concentrations (mg L^{-1}) and the collected volume (L m^{-2}) of open field precipitation (BD), throughfall or stemflow. Stand deposition (TF) was calculated as the sum of throughfall and stemflow deposition.

Drainage fluxes were calculated for the O, A, B and C horizon using the mass balance method (see section 2.4). Soil solution DOC fluxes for the fortnightly sampling periods were calculated as the product of drainage flux and DOC concentration. Monthly soil solution DOC fluxes were calculated as the sum of the two fortnightly fluxes; annual fluxes as the sum of the twelve monthly fluxes. Because a number of data were missing for several evident reasons (e.g. no sampling performed due to snow, or not enough sample volume available for analysis) this would result in an underestimation of DOC fluxes. In order to obtain more realistic DOC fluxes, missing DOC concentrations were interpolated using a logarithmic curve (which gave a better fit than a linear regression) for all measured DOC concentrations during the same year in function of sampling period number. If not enough data were available to obtain a reliable curve ($R^2 < 0.2$), DOC concentrations were interpolated as the average of the previous and the following measured DOC concentration. Missing Na^+ concentrations were interpolated as the average of the previous and the following measured Na^+ concentration. For soil solution DOC concentrations measured in a period without rainfall, no water flux could be

calculated. In that case the DOC flux was interpolated as the average of the previous and the following DOC flux obtained from measured DOC concentrations, if possible weighted by DOC concentration and sample volume. We assumed that DOC fluxes through the C horizon represented C losses below the rooting zone.

4.2.5   Statistical analysis

Data exploration and statistical analysis were performed in S-plus for Windows, version 6.2, and in R (R Core Team, 2012). The nonparametric Seasonal Mann-Kendall Test (Hirsch et al., 1982) was applied to detect monotonic trends in monthly aggregated data for water fluxes, DOC concentrations and DOC fluxes. Trends were evaluated by the significance of Theil-Sen's slope (Sen, 1968). The change (increase or decrease) of DOC concentrations and fluxes was expressed as a percentage in function of the mean value for the 11-year observation period and Theil-Sen's slope:

$$change\ (\%) = \frac{11 \times slope}{mean - \frac{1}{2}(11 \times slope)} \times 100 \tag{1}$$

Cross-site statistics were performed by means of ANOVA/Tukey's range test. The impact of airborne or canopy-derived DOC on soil solution DOC was evaluated by comparing single DOC fluxes in stand precipitation with fluxes in soil solution, using Spearman's rank correlation ('cor.test' function in R) and simple linear regression ('lm' function in R), the latter after natural log transformation of DOC fluxes to obtain normally distributed residuals. Seasonal variation within the data was tested in R by introducing harmonic terms (sine and cosine) in a stepwise regression of the dependent variable y versus time (e.g. Thimonier et al., 2008), in the form:

$$y = c1 + c2 \cdot \sin t + c3 \cdot \cos t + c4 \cdot \sin 2t + c5 \cdot \cos 2t + c6 \cdot \sin 3t + c7 \cdot \cos 3t + c8 \cdot \sin 4t + c9 \cdot \cos 4t + c10 \cdot \sin 5t + c11 \cdot \cos 5t \tag{2}$$

where $t = 2\pi/365 \times (ordinal\ day)$ and $c1 - c11$ are regression coefficients. Sine and cosine terms up to $5t$ were included, which allows the model to show processes which go up or down within a little more than one month. This makes the analysis sensitive enough to reveal the important features of the annual cycle, but not too sensitive to single irregularities.

4.3   **Results**

4.3.1   Long-term trends of DOC

Trends and significances for annual water fluxes, monthly DOC concentrations and DOC fluxes are presented in Table 4.1. The annual precipitation showed substantial year-to-year variation, with wet years in 2002 and 2012 and dry years in 2003 and 2011 (Figure 4.1). In spite of this, annual BD and TF showed no significant trend between 2002 and 2012. Soil water fluxes showed a significant trend at several individual soil layers, but there were no indications for a consequent increase or decline of the soil water flux through the soil profile at any of the plots.

Concentrations of DOC in BD significantly increased at the five plots during the observation period, by 36–110% (Figure 4.2). Fluxes of DOC in BD significantly increased at WIJ and HOE by 31% and 67% respectively, but remained stable at the other plots (Figure 4.3). Stand precipitation DOC concentrations and fluxes did not change significantly at any of the plots.

In the soil solution, DOC concentrations remained stable in the O horizon at HOE and the B horizon at BRA (Figure 4.2). Elsewhere, DOC concentrations significantly increased by 26–130% in the O horizon, 17–44% in the A horizon, 16–103% in the B horizon and 32–146% in the C horizon. Soil solution DOC fluxes through the O horizon remained stable in GON and HOE, but significantly increased by 36–93% at the other three plots (Figure 4.3). Soil solution DOC fluxes through the mineral soil remained stable at BRA, WIJ and GON, but increased significantly in RAV and HOE (except the A horizon at HOE).

Table 4.1 Seasonal Mann-Kendall trends for water fluxes (mm yr^{-1}), DOC concentrations (mg L^{-1}) and DOC fluxes (kg ha^{-1} yr^{-1}) for BD and TF, O horizon and mineral soil layers (2002–2012), with mean annual values, letters (a–e) indicating groups of plots with comparable mean, Theil-Sen's slope (annual change) and significance (ns: not significant, *: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$).

Plot	Sampling Depth (cm)	Water fluxes Mean (mm yr^{-1})	Slope	DOC concentrations Mean (mg L^{-1})	Slope	DOC fluxes Mean (kg ha^{-1} yr^{-1})	Slope
BD							
RAV		923a	ns	2.2a	+0.1***	20.2a	ns
BRA		960a	ns	2.4a	+0.1*	19.0a	ns
WIJ		929a	ns	2.2a	+0.1**	19.0a	+0.5*
GON		838a	ns	2.0a	+0.1***	15.0a	ns
HOE		971a	ns	1.9a	+0.1***	17.0a	+0.8**
TF							
RAV		649ab	ns	17.5a	ns	106.2a	ns
BRA		770a	ns	14.9a	ns	102.8a	ns
WIJ		718ab	ns	7.9c	ns	49.0b	ns
GON		621b	ns	11.2b	ns	60.0b	ns
HOE		766a	ns	7.8c	ns	49.6b	ns
O horizon							
RAV		513ab	ns	41.9a	+0.9*	211.5a	+7.0*
BRA		590a	ns	35.4b	+2.0***	201.3a	+5.6*
WIJ		644a	ns	27.0c	+1.9***	185.1a	+10.7***
GON		431b	ns	35.5b	+1.0**	160.2a	ns
HOE		578a	+17.5*	33.5b	ns	189.6a	ns
A horizon							
RAV	10-25	395a	ns	46.4a	+0.9**	185.4a	+7.0**
BRA	15-25	348a	ns	38.1b	+1.3***	131.7b	ns
WIJ	10-20	355a	-13.5*	35.0c	+1.1***	118.7bc	ns
GON	10-20	328a	ns	25.8d	+0.4**	84.5d	ns
HOE	10-15	398a	-10.2*	22.6e	+0.6***	88.0cd	ns
B horizon							
RAV	30-45	295ab	+13.1**	42.6a	+0.6*	121.5a	+6.0***
BRA	30-55	264b	ns	31.0b	ns	76.5b	ns
WIJ	45-70	253b	ns	19.1c	+0.6***	48.9cd	ns
GON	25-40	314ab	-10.6*	19.7c	+0.5***	57.5bc	ns
HOE	20-30	372a	ns	8.0d	+0.5***	28.7d	+1.0*
C horizon							
RAV	70-95	297ab	+11.9**	19.6b	+0.5***	61.3a	+3.9***
BRA	70-90	268b	-15.5***	21.2a	+0.8***	54.5a	ns
WIJ	75-110	189c	-6.5**	10.4d	+0.4***	19.3b	ns
GON	45-55	208c	ns	13.2c	+0.5***	27.8b	ns
HOE	35-55	367a	ns	8.1e	+0.6***	29.7b	+1.4***
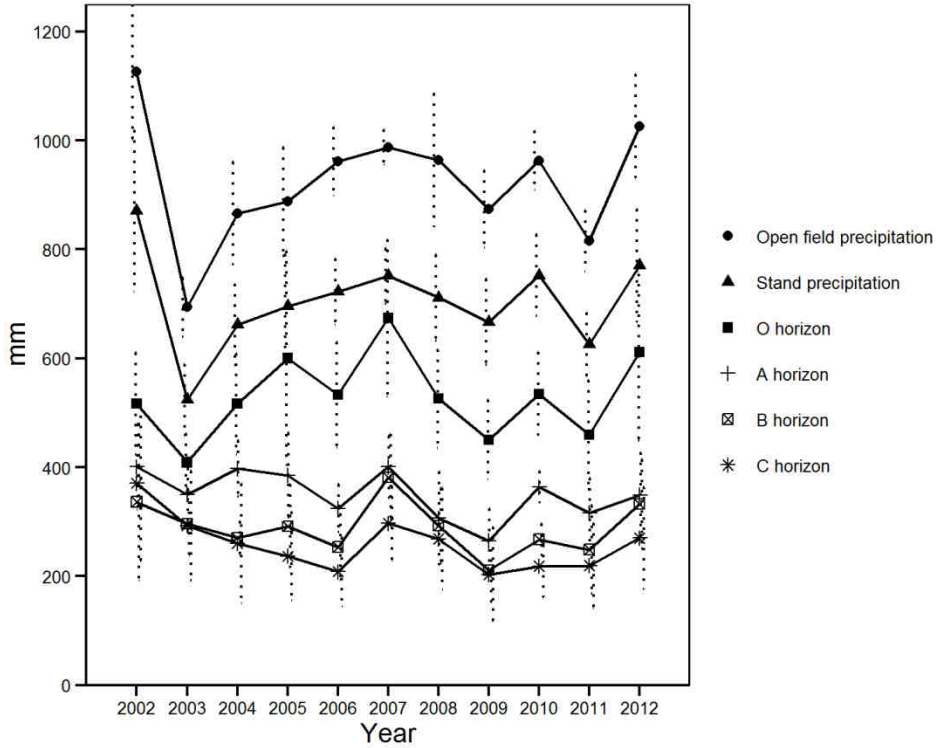
Figure 4.1 Mean annual open field precipitation, stand precipitation (throughfall + stemflow) and soil water flux per depth for the five plots (mm) with standard deviation (dashed bars).
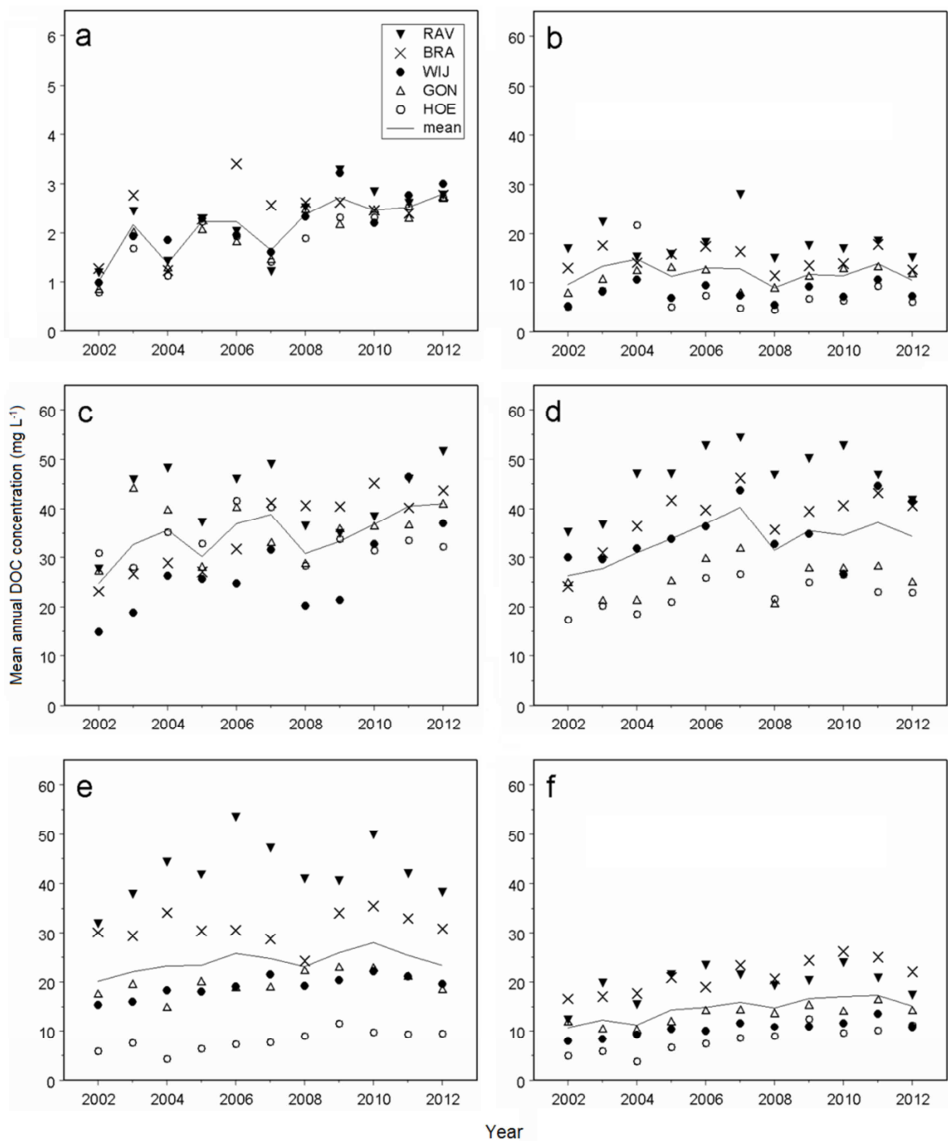
Figure 4.2 Mean annual concentration of DOC (mg L^{-1}) in BD (a), TF (b) O horizon (c), A horizon (d), B horizon (e) and C horizon (f).
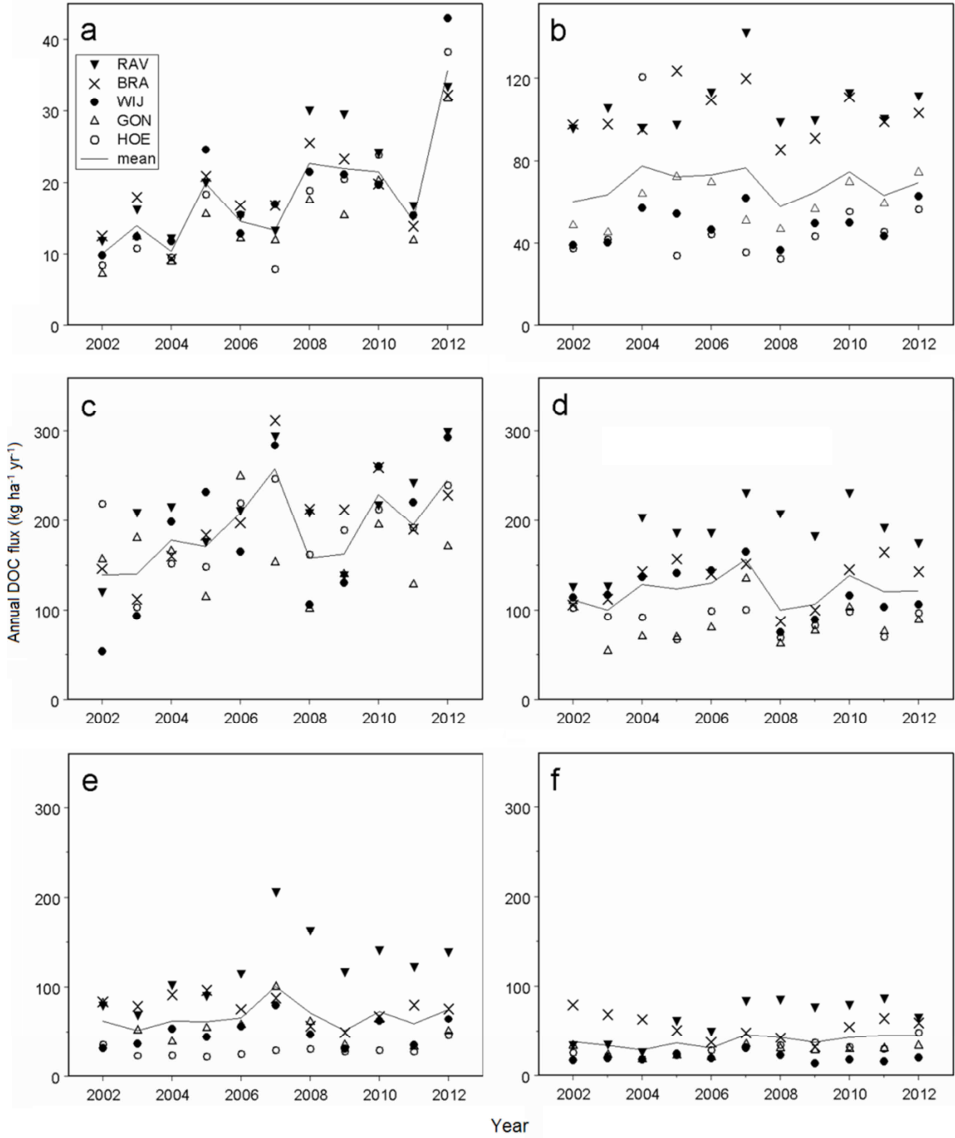
Figure 4.3 Annual flux of DOC (kg ha^{-1} yr^{-1}) for BD (a), TF (b) O horizon (c), A horizon (d), B horizon (e) and C horizon (f).

4.3.2   Within and across-site variability of DOC

Soil solution DOC concentrations and fluxes generally decreased with depth, with an exception for the plots on sandy soils (RAV, BRA and WIJ), where mean annual DOC concentrations were higher in the mineral topsoil than in the organic layer (Table 4.1). Concentrations and fluxes of DOC for TF and soil solution were higher in coniferous than in deciduous plots, and this difference became increasingly important with increasing soil depth. Stand precipitation DOC fluxes were nearly twice as high in coniferous compared to deciduous plots. Accordingly, leaching losses of DOC below the rooting zone were significantly higher in coniferous (55–61 kg C ha^{-1} yr^{-1}) compared to deciduous plots (19–30 kg C ha^{-1} yr^{-1}). These C losses embody 0.12–0.14% and 0.03–0.15% of the C stock in the forest floor and 0.04–0.07% and 0.01–0.03% of the organic C stock in the upper 1 m of the mineral soil in deciduous and coniferous plots respectively (Table 4.2). We found no correlation between C losses and soil organic C stocks.

Table 4.2 Rooting depth (cm) and total organic carbon stock (ton C ha^{-1}) in the forest floor (FFC) and the upper 1 m of the mineral soil (SOC) in the five Level II plots in Flanders (De Vos, 2009).

Plot	FFC (ton C ha^{-1})	SOC (ton C ha^{-1})	Rooting depth (cm)
Coniferous forests			
RAV	52.2	149	185
BRA	38.7	82.5	160
Deciduous forests			
WIJ	64.3	200	170
GON	40.3	132	180
HOE	20.4	93.7	195

4.3.3   Impact of air-borne or canopy-derived DOC

Fluxes of DOC in BD amounted to 9–10% of the estimated annual DOC fluxes through the organic layer, while TF DOC fluxes amounted to 50–51% and 26–37% of the estimated annual DOC fluxes through the organic layer of coniferous and deciduous plots respectively.

Stand precipitation DOC fluxes were strongly (p < 0.001) correlated with soil solution DOC fluxes at all depths in each plot. The linear models showed that 23–24% of the

variance in soil solution DOC fluxes could be explained by stand deposition (Figure 4.4). The slope of regression lines showed little difference between the soil depths (0.50–0.58), while the intercept declined with depth from 1.32 to -0.36, reflecting the removal of DOC by mineralization and sorption towards the C horizon.

Soil solution DOC concentrations and fluxes showed a clear seasonal pattern at all locations, with the highest mean monthly values observed near the end of the growing season, particularly from August till December (Figure 4.5, Figure 4.6 and Figure 4.7). The seasonal variation of DOC concentrations gradually declined with depth, to become no longer significant in the C horizon, while water fluxes and DOC fluxes showed seasonality at all depths (Table 4.3). Fluxes of DOC in BD and TF were highest during late spring and summer (May–August). The seasonal pattern of TF DOC fluxes was most eminent in the deciduous plots, where DOC concentrations showed two peaks: a first one in May around the moment that buds break and leaves are unfolded, and a second one in September just before the start of litterfall.

Table 4.3 Regression models for the seasonal variation of water fluxes, DOC concentrations and DOC fluxes for BD and TF, O, A, B and C horizon, with the number of observations (n), coefficient of determination (R^2) and significance (*: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$).

	Water fluxes			DOC concentrations			DOC fluxes		
	n	R^2	sig.	n	R^2	sig.	n	R^2	sig.
BD	1206	0.08	***	1206	0.12	***	1206	0.09	***
TF	1206	0.08	***	1206	0.20	***	1206	0.11	***
O horizon	1024	0.20	***	1026	0.07	***	1024	0.18	***
A horizon	777	0.20	***	782	0.14	***	777	0.17	***
B horizon	854	0.23	***	871	0.01	*	854	0.19	***
C horizon	843	0.20	***	861	0.004		843	0.16	***
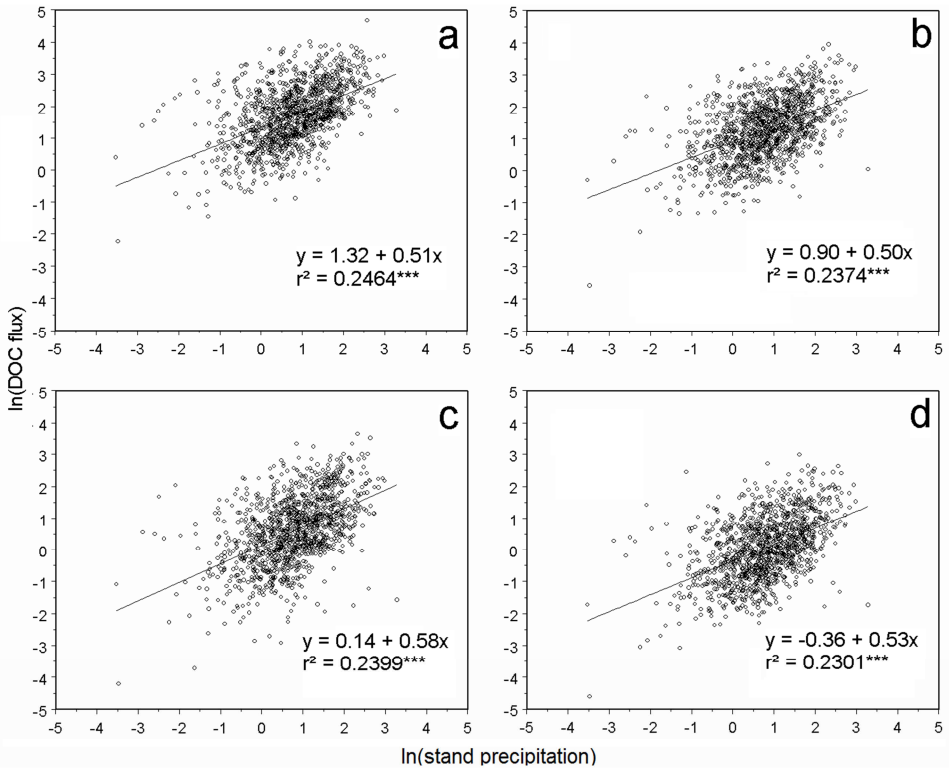
Figure 4.4 Linear models for log-transformed DOC fluxes (kg ha^{-1}) in soil solution of the O horizon (a), A horizon (b), B horizon (c) and C horizon (d) in function of log-transformed stand precipitation (mm).
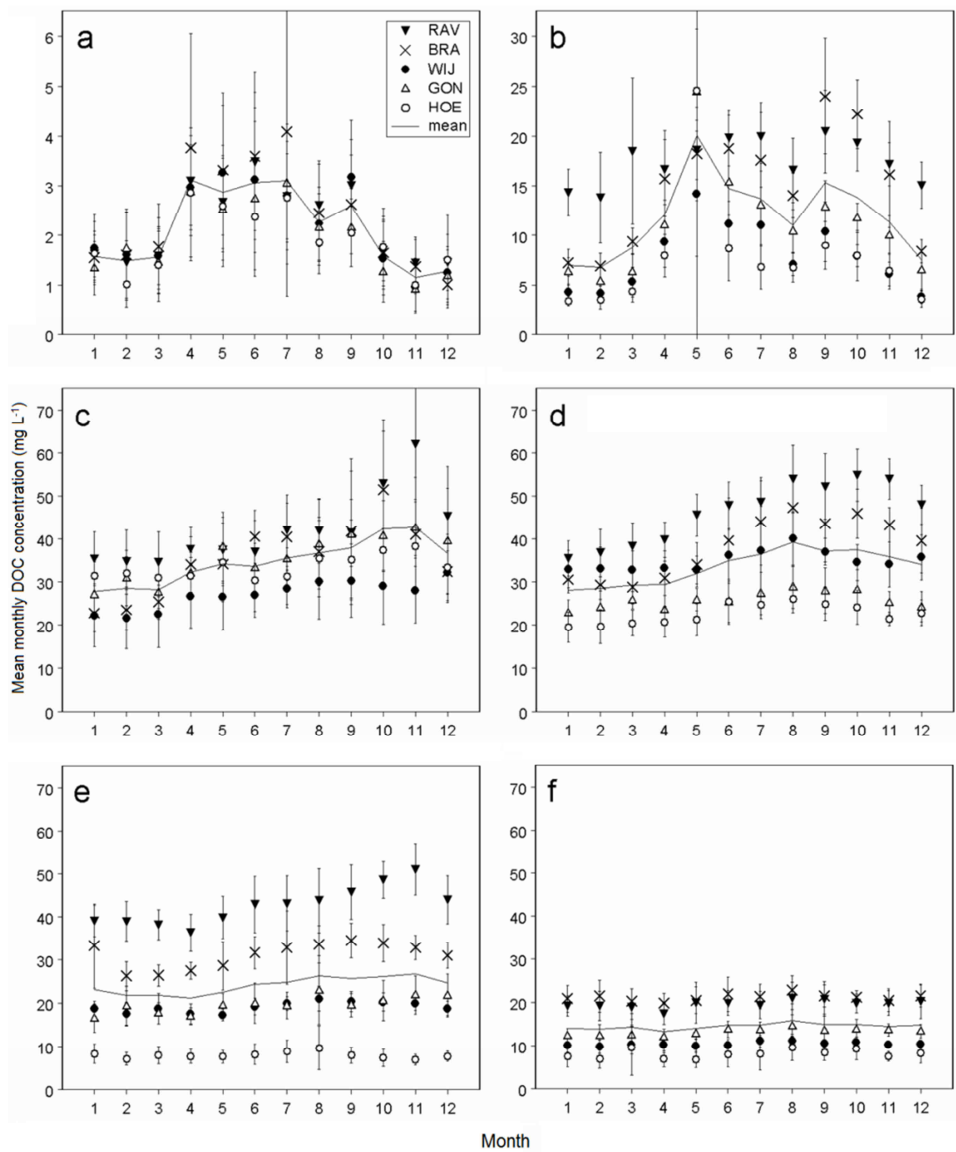
Figure 4.5 Mean monthly DOC concentration (mg L^{-1}) in BD (a), TF (b), and soil solution of the O horizon (c), A horizon (d), B horizon (e) and C horizon (f) (2002–2012). Error bars represent the 95% confidence interval for the original data (before interpolation).
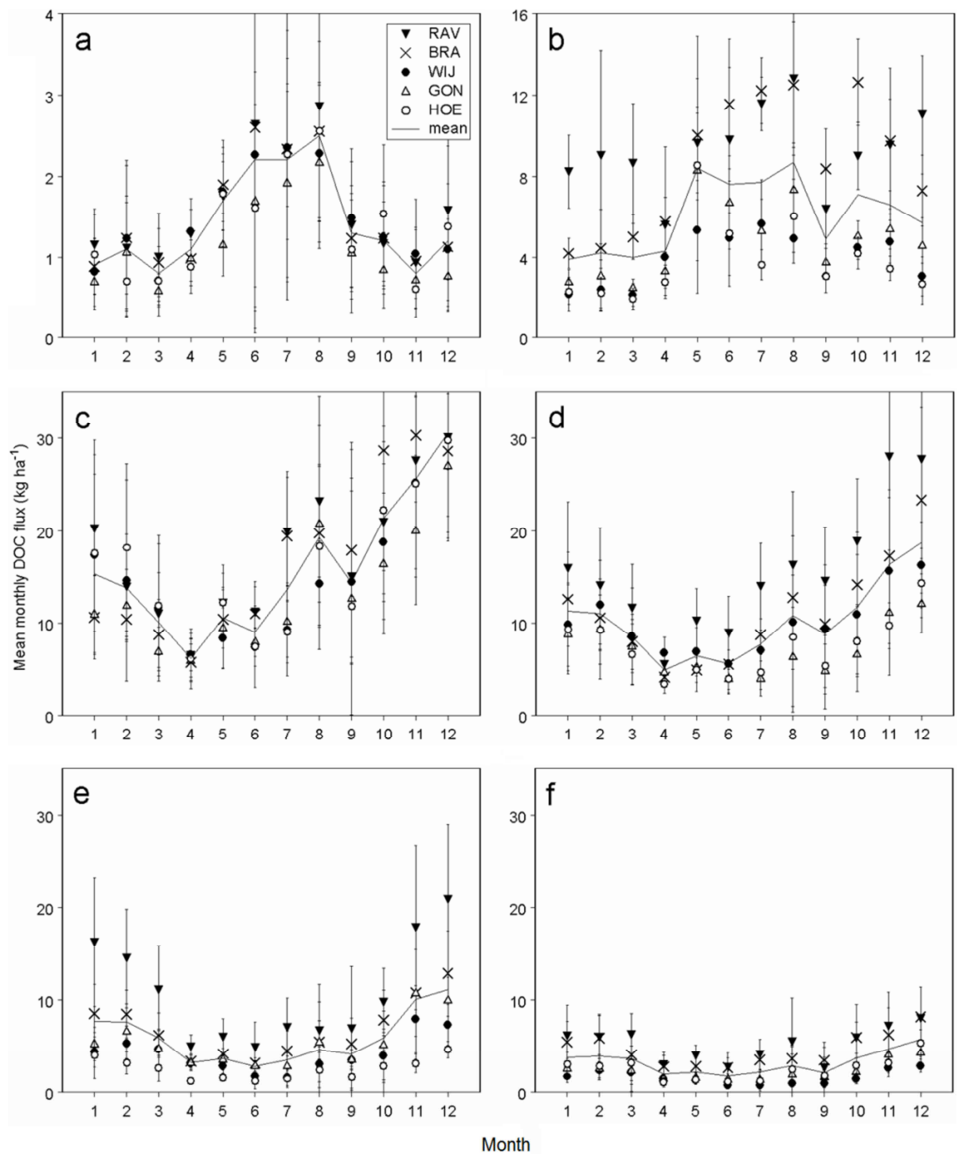
Figure 4.6 Mean monthly DOC flux (kg ha^{-1}) for BD (a), TF (b), and through the O horizon (c), A horizon (d), B horizon (e) and C horizon (f) (2002–2012). Error bars represent the 95% confidence interval for the original data (before interpolation).
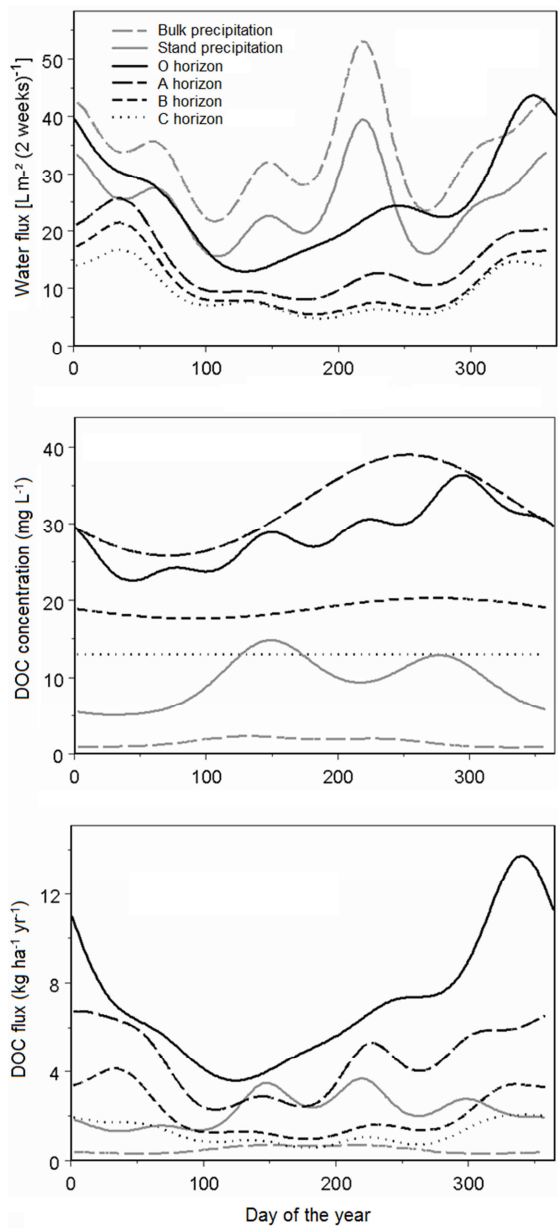
Figure 4.7 Modeled seasonal variation of water fluxes (L m^{-2} (2 weeks)$^{-1}$], DOC concentrations (mg L^{-1}) and DOC fluxes (kg ha^{-1} yr^{-1}) for BD, TF, O horizon, A horizon, B horizon and C horizon.

4.4   **Discussion**

4.4.1   Long-term trends of DOC

The observed increase in soil solution DOC concentrations over the last ten years is in agreement with the recent predominance of increasing trends in soil solution DOC observed in Europe and North America (Freeman et al., 2001; 2004; Monteith et al., 2007), although some studies reported stable or negative trends, particularly at high northern latitudes (e.g. Wu et al., 2010a; Akselsson et al., 2013). The increase in DOC can be basically explained by recovery processes in the soil and soil solution initiated by the overall decline of sulphur depositions (de Wit et al., 2007; Borken et al., 2011; Evans et al., 2012). Past acid conditions have reduced litter decomposition rates, allowing a pool of relatively labile organic matter to accumulate, from which DOC may be generated when acidity decreases (Oulehle and Hruška, 2009). Because atmospheric sulphur depositions and ion concentrations in the soil solution showed a strong and parallel decline at the five plots between 1994 and 2010, the increase in soil solution DOC concentrations can at least partly be explained by recovery from acidification (Verstraeten et al., 2012). The increase in soil solution DOC at the five plots appears to be unrelated to air-borne or canopy-derived DOC, which disproved our hypothesis, since TF DOC concentrations and fluxes remained stable during the observation period.

In the soil solution, DOC fluxes showed less systematic trends than concentrations, which may be explained by the strong dependence of DOC fluxes on water fluxes and the relatively high year-to-year variation in precipitation and soil water fluxes (Neff and Asner, 2001; Buckingham et al., 2008; Gielen et al., 2011). This could imply that longer time series (>11 years) are recommended to study trends in soil solution DOC fluxes. Our hypothesis that soil solution DOC concentrations and fluxes increased during the study period was thus confirmed for concentrations, but less clearly for fluxes.

The concentrations and fluxes of DOC observed at the five plots are in the order of magnitude reported by other studies in temperate forests in Europe (Buckingham et al., 2008; Sleutel et al., 2009; Wu et al., 2010a; Borken et al., 2011; Löfgren and Zetterberg, 2011; Arisci et al., 2012). Carbon leaching losses of up to 61.3 kg ha^{-1} yr^{-1} were recorded, but embody less than 0.05% of measured total 1-m soil organic C stocks (De Vos, 2009). No correlation existed between C losses and soil total organic C stocks, which might be explained by differences in the chemical composition of DOC and SOC between plots.

Data on the chemical composition of DOC in the plots are lacking, but hot-water C pools have been measured (Dr. Bruno De Vos, personal communication). Hot-water C is a part of the total organic C pool that correlates strongly with microbial biomass and is therefore thought to be labile in nature (Sparling et al., 1998; Ghani et al., 2003). A relationship between hot-water C pools and DOC could thus provide information about DOC degradability. However, no correlation was found between annual C losses and hot-water C stocks, which indicates that a considerable part of DOC likely consists of compounds that are not easy degradable.

4.4.2   Within and across-site variability of DOC

The observation that soil solution DOC fluxes, and consequently C losses below the rooting zone, were higher in coniferous compared to deciduous plots, accords with the results of similar studies and could be explained by the interaction between tree species, soil type and pollution climate (Currie and Aber, 1997; Borken et al., 2011; Arisci et al., 2012). Regarding the tree species, DOC levels are generally higher in coniferous forests, primarily due to more intensive leaching of DOC from an evergreen canopy, the higher C:N ratio of needles compared to leaves and the higher mass of the forest floor (Arisci et al., 2012; van den Berg et al., 2012). Regarding the pollution climate, the higher DOC levels in coniferous plots could be related to the higher N deposition in these plots (Guggenberger and Zech, 1993; Sleutel et al., 2009; Verstraeten et al., 2012). Regarding the soil type, soils in the deciduous plots have a higher DOC retention capacity, due to their higher clay content, cation exchange capacity (CEC) and base saturation, providing more sorption sites and higher potential for cation bridging of organic compounds (Guggenberger and Zech, 1993; Kerr and Eimers, 2012).

4.4.3   Impact of air-borne or canopy-derived DOC

The strong correlation that we found between TF DOC fluxes and soil solution DOC fluxes could be explained by their strong dependence on the amount of precipitation, as observed earlier in temperate forest ecosystems in North America and Europe (Michalzik et al., 2001; Neff and Asner, 2001; Buckingham et al., 2008). On the other hand we found that seasonal peaks of DOC in TF and soil solution did not occur simultaneous, which was also observed in Norwegian forests (Wu et al., 2010a). This confirms that the impact of deposition is limited, and that soil solution DOC originates mainly from biologically and/or biochemically mediated processes in the soil compartment, including the activity of

soil biota, soil respiration, root development and root exudation (Yano et al., 2000; Neff and Asner, 2001; Carrara et al., 2004; Buckingham et al., 2008; Futter et al., 2011).

However, several studies point out that the impact of air-borne or canopy-derived DOC could increase in the future (Clark et al., 2009; Vitasse et al., 2009; Pitman et al., 2010; Reyer et al., 2013). In the canopy, the activity of phytophagous insects - especially aphids generating honeydew - can increase DOC levels during summer (Michalzik and Stadler, 2005; Pitman et al., 2010). With the progress of climate change, the intensity of insect attacks is expected to increase, with a possibly more severe impact on the forest C cycle (Clark et al., 2009; Pitman et al., 2010). Climate change also extends the length of the growing season in temperate regions, and according to climate change scenarios may increase the net primary production (CO_2 effect) of forests in Northern Europe (Vitasse et al., 2009; Reyer et al., 2013).

We suggest that the impact of DOC deposition on soil solution DOC concentrations and fluxes will be further examined in the future, preferentially by means of long data series from a larger number of sites within a broader geographical extent, e.g., at the European level. Experimental studies, for example with addition of DOC containing labelled carbon (C^{14}), may provide new insights into this matter.

4.5   **Conclusions**

Concentrations of DOC in the soil solution of forests in Flanders increased between 2002 and 2012 at all plots, while DOC fluxes showed less systematic trends. These trends could not be explained by temporal deposition patterns. Concentrations of DOC and annual C leaching losses below the rooting zone were higher in coniferous compared to deciduous plots but embody less than 0.05% of total 1-m soil organic C stocks. Our results confirmed that air-borne or canopy-derived DOC has a limited impact on soil solution DOC, and that soil solution DOC originates mainly from biologically and/or biochemically mediated processes in the soil compartment.

5 INCREASING TRENDS OF DISSOLVED ORGANIC NITROGEN (DON) IN TEMPERATE FORESTS UNDER RECOVERY FROM ACIDIFICATION IN FLANDERS, BELGIUM

Abstract

We evaluated trends (2005–2013) and patterns of dissolved organic nitrogen (DON) and its ratio with dissolved organic carbon (DOC), DOC:DON in atmospheric deposition and soil solution of five Level II plots of the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) in Flanders, Northern Belgium. The primary aim was to confirm positive postulated trends in DON levels and the DOC:DON ratio under on-going recovery from acidification. The DON concentrations (0.95–1.41 mg L^{-1}) and fluxes (5.6–8.3 kg ha^{-1} yr^{-1}) in throughfall were about twice as high compared to precipitation in the open field (0.40–0.48 mg L^{-1}, 3.0–3.9 kg ha^{-1} yr^{-1}). Annual soil profile leaching losses of DON varied between 1.2–3.7 kg ha^{-1} yr^{-1}. The highest soil DON concentrations and fluxes were observed beneath the O horizon (1.84–2.36 mg L^{-1}, 10.1–12.3 kg ha^{-1} yr^{-1}). Soil solution concentrations and fluxes of DON showed significant increasing trends. Temporarily soil solution DOC:DON rose following an exceptionally long spring drought in 2007, suggesting an effect of drying and rewetting on DOM composition. Further research is needed to test the dependence of DON and the DOC:DON ratio on factors such as latitude, forest cover, length of the growing season, hydrology and topography. Nonetheless, even with considerable variation in soil type, level of base saturation, and soil texture in the five included ICP Forests Level II plots, all data revealed a proportionally larger positive response of DON flux than DOC to recovery from acidification.

5.1   **Introduction**

Atmospheric deposition of inorganic nitrogen (N) and sulphate (SO_4^{2-}) caused N saturation and a fast acidification of temperate forest soils and waters in large parts of Europe and the US during the second half of the 20th century (van Breemen et al., 1984; Aber et al., 1989). This was found to have an impact on dissolved organic matter (DOM) cycling, often resulting in higher concentrations and leaching of DOM (Kalbitz et al., 2000; McDowell et al., 2004; Pregitzer et al., 2004). National policies and international cooperation to abate acidifying emissions implemented since the late 1970's, like the Convention on Long-range Transboundary Air Pollution (CLRTAP), resulted in a significant lowering of acidifying deposition. In European forests, Waldner et al. (2014) observed an overall decrease in non-marine SO_4^{2-} depositions by 6% per year between 2000 and 2010.

Long-term positive trends of surface water dissolved organic carbon (DOC) concentration across Europe, Canada and the US occurred simultaneously (de Wit et al., 2007; Monteith et al., 2007). These positive DOM trends in stream waters and soil solutions of highly acidified forests were mainly linked to the declining non-marine SO_4^{2-} depositions and subsequent initial chemical recovery of the soil solution (de Wit et al., 2007; Monteith et al., 2007; Oulehle et al., 2011). As postulated by Monteith et al. (2007), decreasing soil solution SO_4^{2-} concentrations will lower soil solution ionic strength, leading to an increased solubility of DOM. In addition, the resulting higher pH would increase OM solubility by lowering soil solution concentrations of ionic aluminium (Al^{3+}). For temperate forests, however, negative or indifferent multi-year trends in leachate DOC concentration were seen as well (Monteith et al., 2007; Vanguelova et al., 2010; Borken et al., 2011; Löfgren and Zetterberg, 2011; Oulehle et al., 2011; Akselsson et al., 2013; Verstraeten et al., 2014). Contrary to DOC, still little long-term data exists on DON concentrations and vertical fluxes in temperate forests under recovery from acidification. Mainly so, because monitoring of DON was only recently introduced in forest monitoring networks. Although the concentrations of DON in throughfall water and soil solution are correlated with the concentrations of DOC, since N-containing organic building blocks (proteinaceous or heterocyclic-N) are also comprised in the DOC (Qualls and Haines, 1991; Michalzik et al., 2001; Wu et al., 2010b), it is not clear to what extent DON concentrations follow trends in DOC. Oulehle et al. (2011) observed parallel trends in soil solution DOC and DON of a spruce forest showing acidification recovery in the Czech Republic. Vanguelova et al.

(2010) found that a positive trend of DOC was not always coupled to a positive trend of DON at 10 ICP Forests Level II sites in the UK. It should be noted though, that both studies were shorter than nine years identified as minimum for distinguishing clear trends in DOM (Waldner et al., 2014).

When investigating deposition effects on DON, also account has to be taken of evolutions in inorganic N deposition, as it also impacts DOM cycling (Currie et al., 1996; Campbell et al., 2000; McDowell et al., 2004; Pregitzer et al., 2004; Brookshire et al., 2007). In European forests, inorganic N depositions decreased by 2% per year between 2000 and 2010, but only in certain regions, while other regions showed stable or increasing N depositions (Waldner et al., 2014). It is still unclear, however, if an increase in the DOC:DON ratio could be expected under recovery from N deposition.

Finally, increasing trends of DON have also been linked to climate warming (Vanguelova et al., 2010), with often observed positive correlation between the concentrations of DOC and DON in throughfall and air temperature (Solinger et al., 2001; Sleutel et al., 2009; Wu et al., 2010b). Increasing throughfall inputs of DON could explain positive DON trends in soil solution (Vanguelova et al., 2010). Throughfall inputs are an important source for DOM in soil solution, and contribute relatively more to DON than to DOC in soil solution (Guggenberger and Zech, 1994; Michalzik et al., 2001; Solinger et al., 2001; Sleutel et al., 2009). Higher air temperatures could increase the activity of herbivorous insects in the canopy, which could lead to higher throughfall fluxes of DOM (Michalzik and Stadler, 2005; Pitman et al., 2010). Higher soil temperatures also stimulate decomposition and mineralization processes, which could increase DOC and DON leaching from the forest floor (Andersson et al., 2000; Michalzik et al., 2001).

The complex interplay of biological and physico-chemical factors that influence DON and DOC cycling, make it difficult to predict the net effects of shifts in climate or deposition onto vertical DOM balances. Long-term data from intensive monitoring plots accounting for all these potential environmental drivers, are crucial to forward our understanding of changing DOC and DON fluxes in forests. We monitored the concentrations and fluxes of DON and DOC in the deposition and soil solution of five ICP Forests intensive monitoring plots (Level II) in Flanders (Belgium) and examined the data for unique long-term trends (2005–2013) and patterns of DON and DOC:DON. Positive DOC trends were recently observed at the five plots following a sharp decline in atmospheric SO_4^{2-} deposition (Verstraeten et al., 2012; 2014). The first objective of this study was to check to what

extent trends in DON followed trends in DOC and we hypothesized that concentrations and fluxes of DON in the deposition and soil solution followed the DOC trends. Since N-rich DOM compounds generally have a lower reactivity with Fe and Al hydroxides, a pH control on DON solubility is probably smaller than for DOC. Hence, we hypothesized that recovery from acidification disproportionally favours DOC dissolution compared to DON and the DOC:DON ratio would increase over time. Under field conditions, however, pH-dependent processes like microbial degradation and plant growth also govern DOC and DON levels, complicating the purely abiotic pH-DOM-solubility relation. The relevance of abiotic and biotic DOM transformations is furthermore very much depth-distributed, e.g. depending on Fe and Al content of soil horizons. A second objective thus was to firstly detect and interpret change in the DOC:DON ratio in the five ICP Forests Level II plots by means of an extensive 9-year fortnightly dataset.

5.2 **Materials and Methods**

5.2.1 Study area

Five plots of the ICP Forests intensive monitoring network (Level II) in Flanders, northern Belgium, were included in this study. More details about these Level II plots are given in section 2.1.

5.2.2 Sample collection and measurements

Sampling of throughfall, stemflow and soil solution was carried out fortnightly from January 2005 till December 2013. A detailed description of the methods used for deposition sampling is given in section 2.2.1 and for soil solution sampling in section 2.2.2.

5.2.3 Chemical analysis

A description of the methods used for sample pre-treatment and for the determination of pH and the concentrations (mg L^{-1}) of DOC, Total Kjeldahl nitrogen (TKN), ammonium (NH_4^+) and sodium (Na^+) on the collected samples of throughfall, stemflow and soil solution is given in section 2.3.1.

5.2.4   Data handling

Concentrations of DOC were taken from a previous study for 2005–2012 (Verstraeten et al., 2014), and were supplemented with new data for 2013. Concentrations of DON were calculated as TKN – NH_4^+. The molar ratio of DOC and DON concentrations, DOC:DON, was calculated for each sample for which both concentrations were measured. Deposition fluxes of DON and DOC (kg ha^{-1}) were calculated as the product of concentration (mg L^{-1}) and the collected volume (L m^{-2}) of precipitation in the open field (BD) and below canopy (throughfall + stemflow, further denoted as TF). Drainage fluxes were calculated for each depth using the sodium mass balance method (see section 2.4). Soil solution DON and DOC fluxes (kg ha^{-1}) for the fortnightly sampling periods were calculated as the product of water flux (L m^{-2}) and concentration (mg L^{-1}). Monthly DON and DOC fluxes were calculated as the sum of the two fortnightly fluxes and annual fluxes as the sum of the twelve monthly fluxes. Missing data (for several evident reasons, e.g., no sampling performed due to snow, or insufficient sample volume available for analysis) would result in an underestimation of DON and DOC fluxes. Missing concentrations were interpolated to correct for this as follows. DOC concentrations in a given year were interpolated using a logarithmic curve (which gave a better fit than a linear regression) for all measured DOC concentrations in function of sampling period number in that year. In case not enough data were available or DOC concentrations were still high in January following the peak of DOC concentrations at the end of the previous year, DOC concentrations were calculated as the average concentration of the measurements preceding and following the missing value. For soil solution DON and DOC concentrations measured in a period without rainfall, no drainage flux could be determined. In that case the drainage flux was interpolated as the average of the previous and the following drainage flux obtained from measured concentrations, if possible weighted by concentration and sample volume. We assumed that DON fluxes through the C horizon represented organic N losses below the rooting zone and thus lost from the ecosystem.

5.2.5   Statistical analysis

Data exploration and statistical analysis were performed in R (R Core Team, 2014). The nonparametric Seasonal Mann-Kendall Test (Hirsch et al., 1982) included in the 'rkt' package (Marchetto, 2015) was applied to detect monotonic trends in DON concentrations, DON fluxes, the DOC:DON ratio, pH (2005–2013) and temperature (1996–2013). The rate of annual change (increase or decrease) was expressed as a

percentage in function of Theil-Sen's slope (% per year). Since DON concentrations were not normally distributed (evaluated using the Shapiro-Wilk test included in the 'stats' package), cross-site statistics (for inter-comparison of sites) were performed by means of the non-parametric Kruskalmc test (Multiple comparison test after Kruskal-Wallis) included in the 'pgirmess' package (Giraudoux, 2015). Correlations between fortnightly measured concentrations of DOC or DON and mean air or soil temperature during the period since the previous sampling were evaluated using the Spearman's rank correlation test included in the 'stats' package.

5.3   **Results**

5.3.1   Trends and patterns of DON

In BD, mean annual concentrations (0.40–0.48 mg L^{-1}) and fluxes (3.0–3.9 kg ha^{-1} yr^{-1}) of DON were comparable among the five studied Level II plots (Table 5.1). In TF, mean annual concentrations (0.95–1.41 mg L^{-1}) and fluxes (5.6–8.3 kg ha^{-1} yr^{-1}) of DON were respectively 2.8 and 1.9 times higher than in BD. Fluxes of DON in TF were somewhat higher in the coniferous plots. In the O horizon we observed the highest mean annual DON concentrations (1.84–2.36 mg L^{-1}) and fluxes (10.1–12.3 kg ha^{-1} yr^{-1}). In the mineral soil, DON levels decreased gradually with soil depth from the A till the C horizon. Annual leaching losses of DON (i.e. leaching of DON from the C horizon) were 1.2–3.7 kg ha^{-1} yr^{-1}, representing less than 0.1% of the total soil organic N stock to 1 m depth (Table 5.2).

Concentrations and fluxes of DON in BD were slightly higher during the growing season (from May to August) compared to the rest of the year (Figure 5.1 and Figure 5.2). In TF we observed a more explicit seasonal pattern, with a marked peak of DON concentrations in May, especially in the deciduous plots, and elevated DON fluxes from May till August in all plots. In the soil solution the highest DON fluxes were observed at the end of the year, i.e. when rainfall was abundant.

Table 5.1 Seasonal Mann-Kendall trends (2005–2013) for water fluxes (mm yr^{-1}), DON concentrations (mg L^{-1}), DON fluxes (kg ha^{-1} yr^{-1}) and the molar DOC:DON ratio, with mean annual values, 10th and 90th percentile for concentrations, mean annual values for fluxes, median values for DOC:DON, Theil-Sen's slope (annual change) and significance (ns: not significant, (*): p < 0.1, *: p < 0.05, **: p < 0.01, ***: p < 0.001). Letters (a–d) show plots with comparable mean within groups/layers. The right column shows the significance of Spearman's rank correlation (ρ_S) between DOC and DON concentrations.

Plot	Sampli Depth[†] (cm)	Water fluxes Mean (mm yr^{-1})	Slope	DON concentrations Mean (mg L^{-1})	P10	P90	Slope	DON fluxes Mean (kg ha^{-1} yr^{-1})	Slope	DOC:DON (molar) Median (–)	Slope	ρ_S
BD												
RAV		935a	ns	0.48a	0.09	0.84	ns	3.9a	ns	6.1a	-0.28(*)	ns
BRA		947a	ns	0.40a	0.07	0.81	ns	3.3a	ns	6.8a	ns	*
WIJ		947a	ns	0.46a	0.09	0.86	+0.02(*)	3.8a	ns	6.2a	ns	ns
GON		855a	ns	0.41a	0.09	0.81	ns	3.0a	ns	6.0a	ns	ns
HOE		959a	ns	0.40a	0.10	0.73	ns	3.4a	ns	5.9a	ns	*
TF												
RAV		667a	ns	1.37c	0.32	2.29	+0.06**	8.3b	ns	15.3b	-1.08**	ns
BRA		755a	ns	1.08b	0.28	2.09	+0.05**	7.0b	+0.18(*)	16.3b	-0.84***	**
WIJ		727a	ns	1.05ab	0.31	1.92	+0.04**	5.6ab	+0.21*	9.5a	-0.38*	**
GON		622a	ns	1.41bc	0.34	2.42	+0.08***	6.3ab	+0.31**	10.3a	-0.72***	ns
HOE		764a	ns	0.95a	0.17	1.87	+0.06***	5.9a	+0.36***	9.4a	-0.48**	***
O horizon												
RAV		536ab	ns	2.09ab	0.88	3.28	+0.18***	10.7a	+0.93***	24.4bc	-1.72***	***
BRA		569ab	-17*	2.14ab	0.69	4.14	+0.18***	10.7a	+0.40*	25.6c	-1.73**	***
WIJ		708b	ns	1.84a	0.59	2.97	+0.19***	12.3a	+1.07***	21.4ab	-1.64**	(*)
GON		435a	ns	2.36b	0.83	4.21	+0.22***	10.1a	+0.64***	18.3a	-1.42*	**
HOE		584b	+24*	2.06ab	1.07	3.10	+0.11***	11.1a	+0.94***	20.4a	-1.56***	**

[†]: the C horizons are in fact deeper than the sampling depths

Table 5.1 continued.

Plot	Sapling Depth[†] (cm)	Water fluxes Mean (mm yr⁻¹)	Slope	DON concentrations Mean (mg L⁻¹)	P10	P90	Slope	DON fluxes Mean (kg ha⁻¹ yr⁻¹)	Slope	DOC:DON (molar) Median (–)	Slope	ρ_S
A horizon												
RAV	10–25	427a	ns	1.79c	0.82	2.65	+0.09***	7.9c	+0.38**	34.8c	-2.98***	ns
BRA	15–25	330a	ns	1.68bc	0.92	2.50	+0.08**	5.6bc	+0.24**	31.6bc	-1.19(*)	ns
WIJ	10–20	330a	ns	1.46b	0.71	2.28	+0.13***	4.3ab	ns	34.0bc	-2.68*	*
GON	10–20	334a	ns	2.00c	0.72	2.98	+0.09**	6.5c	+0.25*	16.3a	-1.31**	ns
HOE	10–15	359a	ns	1.05a	0.61	1.58	+0.06***	4.0a	+0.14**	28.3ab	-1.77***	***
B horizon												
RAV	30–45	350ab	ns	1.58c	0.67	2.40	+0.06(*)	5.5b	+0.22**	31.7d	-2.50**	***
BRA	30–55	249a	ns	1.33c	0.67	2.00	+0.06**	3.4b	+0.07(*)	27.1cd	-1.09*	***
WIJ	45–70	257a	ns	0.90b	0.44	1.35	+0.02*	2.1a	ns	25.8c	-0.87*	***
GON	25–40	303ab	ns	1.45c	0.44	2.20	+0.05*	4.2b	+0.11(*)	15.8b	-0.84*	***
HOE	20–30	359b	ns	0.72a	0.33	1.14	+0.06***	2.5a	+0.12**	14.8a	ns	***
C horizon												
RAV	70–95	333b	ns	1.05b	0.42	1.63	+0.04(*)	3.7c	ns	24.0b	-2.14***	**
BRA	70–90	220a	ns	1.13b	0.47	1.80	+0.04*	2.5c	ns	22.9b	ns	**
WIJ	75–110	181a	-4(*)	0.66a	0.23	1.03	+0.02*	1.2a	ns	19.4ab	ns	***
GON	45–55	197a	ns	1.14b	0.37	1.95	ns	2.3bc	ns	15.3a	ns	**
HOE	35–55	344b	ns	0.73a	0.34	1.14	+0.04*	2.1b	+0.13***	15.9a	ns	***

[†]: the C horizons are in fact deeper than the sampling depths

Table 5.2 Total organic N stock (ton N ha^{-1}) for the forest floor (FFN) and the upper 1 m of the mineral soil (SON) in the five Level II plots in Flanders (Fleck et al., 2016).

Plot	FFN (ton N ha^{-1})	SON (ton N ha^{-1})
Coniferous forests		
RAV	1.58	5.2
BRA	1.26	3.0
Deciduous forests		
WIJ	2.67	10.4
GON	1.58	10.9
HOE	0.84	7.7

The amount of precipitation and the drainage fluxes exhibited a certain inter-annual variation (Figure 5.A**1**), but did not significantly change between 2005 and 2013 (Table 5.1). Concentrations and fluxes of DON in BD were stable (Table 5.2, Figure 5.A2 and Figure 5.A3). In TF, DON concentrations and fluxes increased significantly in all plots by 3–9% per year, except fluxes in RAV. In the O horizon, a general increase in DON concentrations (7–19% per year) and DON fluxes (4–14% per year) was observed. Also in the A, B and C horizons DON concentrations and fluxes generally tended to increase, but the magnitude of the increase and the number of significant differences diminished gradually with soil depth. Only at the HOE site a significant increase in DON losses below the rooting zone was observed.

At the BRA site, the concentrations of DON and DOC in TF showed a strong positive correlation ($p < 0.001$) with air temperature. Soil solution DOC concentrations in the A horizon also showed a strong positive correlation ($p < 0.001$) with soil temperature, while soil solution DON concentrations in the A horizon were not correlated with soil temperature. There was no significant change in air temperature during the observation period (Figure 5.A4).
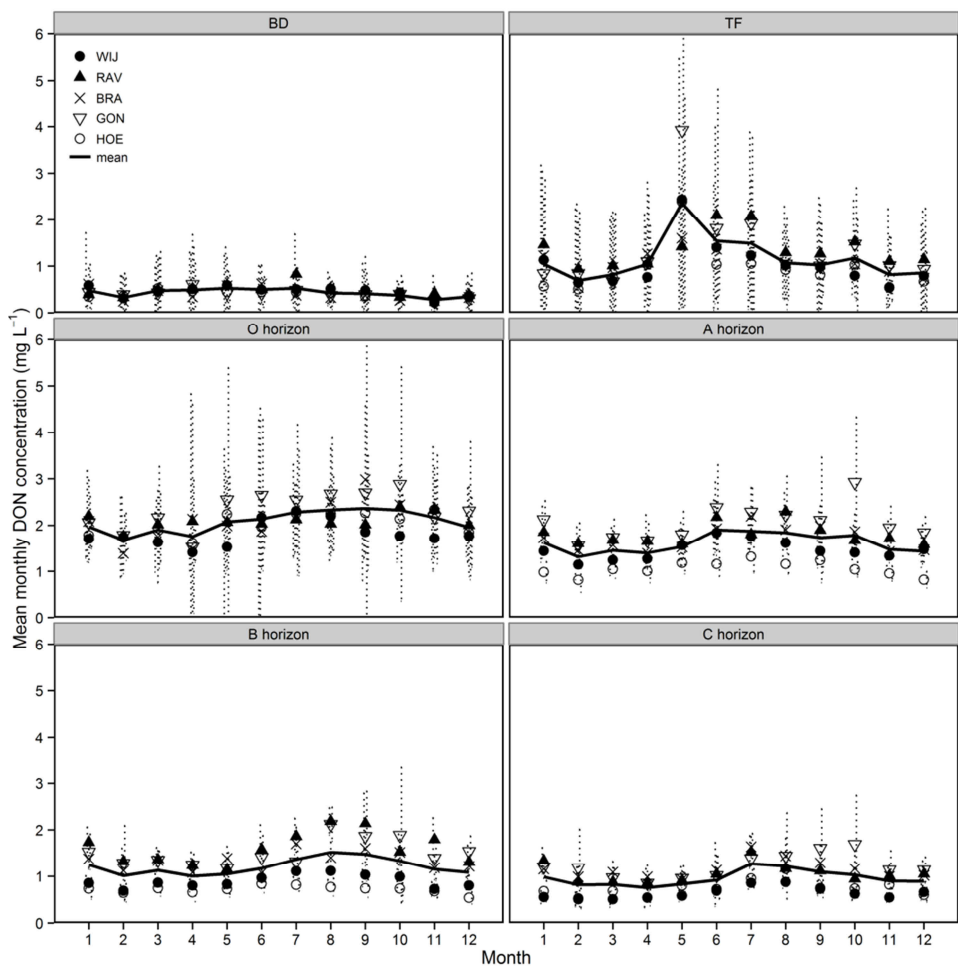
Figure 5.1 Mean monthly DON concentration (mg L^{-1}) in deposition and soil solution (2005–2013) with 95% confidence interval based on the propagation of errors (dashed bars).
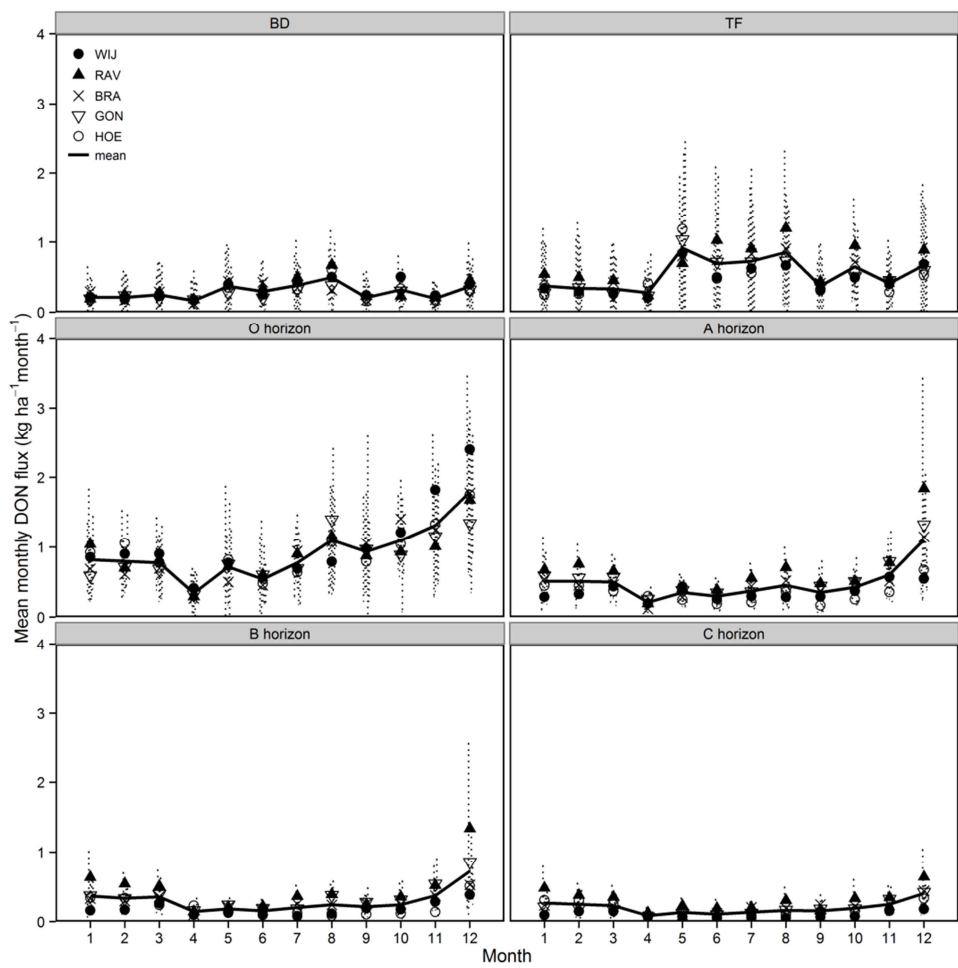
Figure 5.2 Mean monthly DON flux (kg ha^{-1} month^{-1}) in deposition and soil solution (2005–2013) with 95% confidence interval based on the propagation of errors (dashed bars).

5.3.2   Trends and patterns of the DOC:DON ratio

In BD, the DOC:DON ratio was comparable among plots (median 5.9–6.8) (Table 5.1). In TF, the DOC:DON ratio was higher in coniferous plots (median 15.3–16.3) than in deciduous plots (median 9.4–10.3). In the soil solution, the DOC:DON ratio increased with depth from the O horizon (median 20.4–25.6) to the A horizon (median 28.3–34.8) in all plots except GON (median 18.3–16.3). In the mineral soil, the DOC:DON ratio decreased with depth (median 15.3–24.0 in the C horizon) in all plots. Overall, the DOC:DON ratio in soil solution was higher in the plots with a sandy soil texture (RAV, BRA, WIJ) than in the plots with a more silt loam texture (Table 2.2). In TF and in the O horizon, the DOC:DON ratio was somewhat higher near the end of the growing season, while the DOC:DON ratio showed no clear seasonal pattern in BD and in the mineral soil (Figure 5.3).

The concentrations of DOC and DON were weakly correlated in BD, while a strong correlation was observed in TF at three plots (Table 5.1). In the soil solution, concentrations of DOC and DON showed an overall strong correlation, except in the A horizon.

In BD, the DOC:DON ratio remained nearly stable between 2005 and 2013, while the DOC:DON ratio decreased overall in TF and in the soil solution (Table 5.1, Figure 5.A**5**). The DOC:DON ratio in soil solution peaked in 2007, followed by more or less stable values thereafter.

Soil solution pH showed an overall increasing trend between 2005 and 2013, except in the O horizon in RAV and BRA and in the A horizon in HOE (Figure 5.A6).
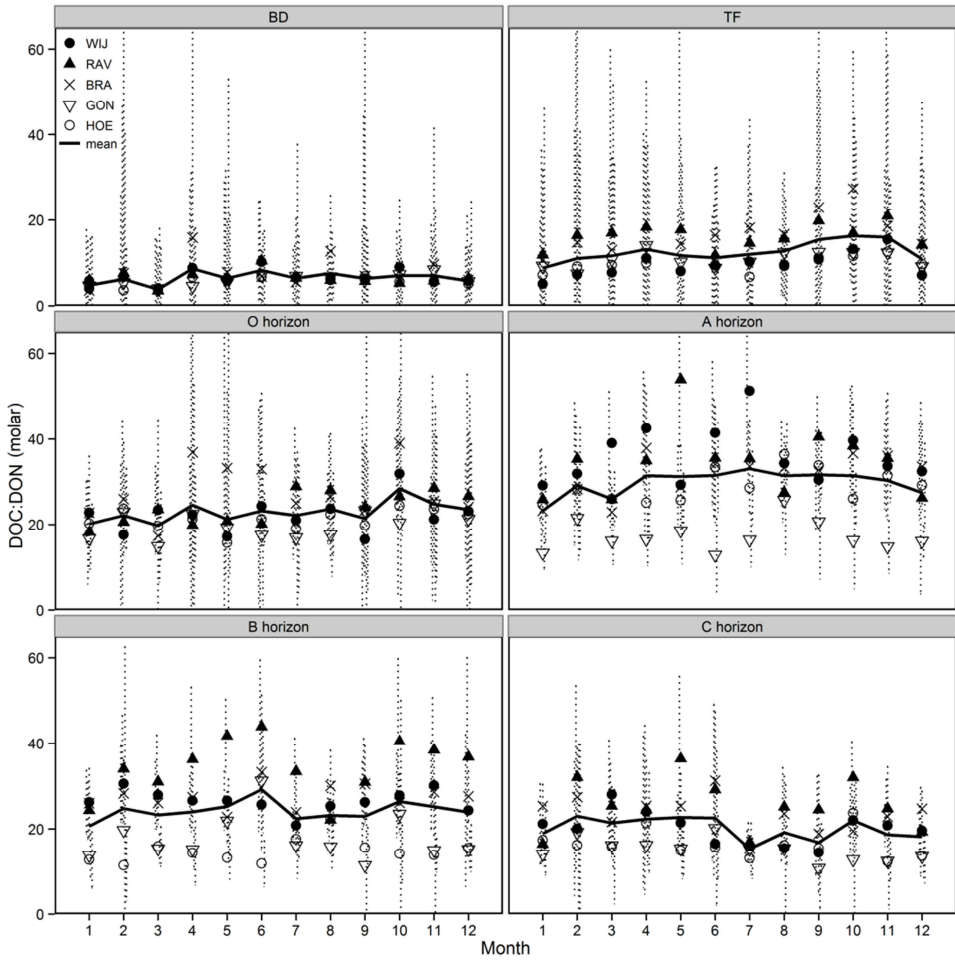
Figure 5.3 Median monthly DOC:DON ratio (molar) in deposition and soil solution (2005–2013) with 95% confidence interval based on the propagation of errors (dashed bars).

5.4   **Discussion**

Despite the wide scientific interest for DON concentrations and fluxes in temperate forests during the past decades (Kalbitz et al., 2000; Michalzik et al., 2001), monitoring of DON concentrations was implemented only recently in forest monitoring networks. The number of published long-term data series on DON concentrations and fluxes is therefore very limited and published time series were often shorter than the minimum of nine years that is recommended to be able to detect clear trends (Vanguelova et al., 2010; Oulehle et al., 2011; Waldner et al., 2014). Our unique 9-year time series of DON concentrations and fluxes in five temperate forests in a high deposition area brings new insights into this matter.

Overall, the concentrations and fluxes of DON in the deposition and soil solution of the five plots were in the middle or higher range of the levels that have been observed at other temperate forests in northwestern and central Europe and eastern US (Michalzik et al., 2001; Sleutel et al., 2009; Vanguelova et al., 2010; Wu et al., 2010b; Oulehle et al., 2011). The DOC:DON ratios that were observed in BD were in the lower range of those reported in similar published studies (Michalzik and Matzner, 1999; Campbell et al., 2000; Solinger et al., 2001), probably due to the relatively high atmospheric DON depositions. The higher DOC:DON in TF in coniferous plots compared to deciduous plots could be attributed to the higher C:N ratio of needles compared to leaves (Cools et al., 2014).

The concentrations and fluxes of DON were stable in BD, but increased in TF during the monitoring period, in contrast with the increase in DOC concentrations in BD and the stable DOC concentrations and fluxes in TF that was observed at the five plots between 2002 and 2012 (Verstraeten et al., 2014). On the other hand, we observed a parallel increase in DON and DOC levels in soil solution. Hence, our hypothesis that trends of DON follow the trends of DOC, was confirmed for soil solution but not for deposition.

The observed increase in DON concentrations and fluxes in the soil solution is in agreement with the predominantly increasing trends of DOC levels observed in forest soils and connected aquatic ecosystems in the central parts of Europe and eastern US (e.g. de Wit et al., 2007; Monteith et al., 2007; Vanguelova et al., 2010; Oulehle et al., 2011). DOC and DON form a crucial link between terrestrial and aquatic carbon and N cycles and contribute significantly to aquatic fluxes of carbon dioxide (CO_2) to the atmosphere (Battin et al., 2009; Lapierre et al., 2013; Regnier et al., 2013). But annual

leaching losses of DON below the deepest horizon considered (1.2–3.7 kg ha^{-1} yr^{-1}) represented less than 0.1% of the total soil organic N stock to 1 m depth and increased only at one of the five plots. Moreover, DON leaching losses were much lower than DOC losses which amounted to 19–61 kg ha^{-1} yr^{-1} at the five plots (Verstraeten et al., 2014), meaning that the impact of DON leaching on the water quality of connected surface waters is probably limited compared to DOC leaching.

A possible explanation for the increase in DON and DOC levels is the significant decline of atmospheric SO_4^{2-} depositions at the five plots between 1994 and 2010 (Verstraeten et al., 2012). At a number of intensive monitoring plots in European temperate forests, including the five Level II plots studied, the decline of atmospheric SO_4^{2-} depositions was followed by an initial chemical recovery of the soil solution, indicated by an increase in pH (Figure 5.A6) and a decrease in SO_4^{2-} and Al^{3+} concentrations (Vanguelova et al., 2010; Oulehle et al., 2011; Verstraeten et al., 2012). As postulated by Monteith et al. (2007) decreasing soil solution SO_4^{2-} concentrations result in lower soil solution ionic strength, leading to an increased solubility of DOM. In addition, ionic Al in soil is known to coagulate DOM, thereby causing precipitation of DOM. Increasing pH therefore also indirectly increases OM solubility by lowering soil solution concentration of Al^{3+}. At the low pH-$CaCl_2$ of about 3 of the mineral horizons (Table 2.2), i.e. in the low end of the Al buffer range, a relatively small increase in pH could strongly reduce Al solubility and therefore promote OM solubility. Hence, the increase in DON in soil solution could be attributed to multiple interlinked abiotic processes, viz. the increase in pH, lowered soil solution Al^{3+} levels and lower SO_4^{2-} concentrations and ionic strength. Trends in the DOC:DON ratio were mostly negative, disproving our hypothesis that recovery from acidification would disproportionally favor the dissolution of DOC relative to DON.

The level of N loading was found to be positively correlated with DON concentration and negatively with the DOC:DON ratio, suggesting that inorganic N can be transformed into DON, as previously postulated (Currie et al., 1996; Campbell et al., 2000; McDowell et al., 2004; Pregitzer et al., 2004; Brookshire et al., 2007). Inorganic N deposition and NO_3^- leaching decreased at the five plots (Verstraeten et al., 2012). Since we observed increasing trends of DON and mostly decreasing DOC:DON in TF and soil solution, we found no cues that DON levels and DOC:DON ratios were influenced by inorganic N deposition at the five plots.

DON was furthermore enriched in DOM with depth and followed the decrease in the soil C:N ratio with depth (Table 2.2). Considering the very low unfavorable pH of the soil mineral horizons (pH-$CaCl_2$ was close to 3), it seems unlikely that microbial consumption of C explains decreasing DOC:DON ratios with depth. Instead, progressively lower DOC:DON ratio is likely explained by selective sorption of DOC upon leaching through mineral soil horizons, because N-rich DOM compounds often have a lower reactivity with iron (Fe) and Al hydroxides compared to N-poor DOM compounds (Qualls et al., 1991; Vandenbruwane et al., 2007; Scott and Rothstein, 2014). In line, at the GON site, the overall low DOC:DON ratios match the more loamy soil texture (higher clay content in the mineral soil) with 4–10 times higher cation exchange capacity, and thus higher sorption capacity of the soil compared to the other plots with a more sandy texture (Table 2.2).

DOM composition was also influenced by temporal variation in hydrological conditions. The DOC:DON ratio in soil solution peaked in 2007 (Figure 5.A**5**), a year characterized by exceptional spring drought followed by abundant rainfall during summer. Clearly in all five sites this sudden rewetting after 37 days of drying temporarily promoted DOC losses but lowered DON losses. Considering predicted global changes in precipitation and evapotranspiration, soil drying and rewetting will likely increase in the next decades (Borken and Matzner, 2009), with possible high temporal DOC leaching.

Although DOC and DON concentrations in water samples are negatively correlated with precipitation through dilution (Michalzik and Matzner, 1999; Sleutel et al., 2009), the seasonal peak in May of DON concentrations in TF in the deciduous plots could not be explained by differences in the monthly precipitation (Figure 5.A**1**). This peak coincided with the dispersal of N-rich pollen, bud burst and the fall of bud scales from oak and beech trees, which could explain the darker, brownish color of water samples from TF and stemflow during this month. Fluxes of DON in TF depended strongly on precipitation, which was highest in August and December and lowest in January and April (Figure 5.A**1**), in accordance with the 30-year average of monthly precipitation in Belgium (www.meteo.be). Our results confirmed that the canopy functions as an important source of DON and DOC in temperate forests (Michalzik et al., 2001), and we observed that particularly spring phenology had a considerable impact on TF DON concentrations and fluxes in deciduous forests, while the impact of autumn phenology (leaf senescence and fall), typically around October-November, was more limited. Given that DON fluxes showed no trend in BD, suggesting stable atmospheric DON inputs, the increase in DON levels in TF could likely be explained by intensified DON leaching from the canopy. The

positive correlation between DOC and DON concentrations in TF and air temperatures at the BRA site confirmed the role of air temperature as a driver of DOM in throughfall water (Solinger et al., 2001; Sleutel et al., 2009; Wu et al., 2010b). A possible explanation is that higher temperatures may stimulate microbial activity and insect herbivore activity in the canopy, which are known to enhance DOM leaching with TF (Michalzik and Stadler, 2005; Pitman et al., 2010). Therefore, a future with climate warming could result in higher DOM leaching from the canopy. The DOM in TF consists for a large part of easily decomposable compounds, which could act as co-substrates or promoters for decomposition and mineralization processes of organic matter in the forest floor (Guggenberger and Zech, 1994). Therefore, increased leaching of DON from the canopy may help to explain the increase in DON levels in the upper soil layers (Michalzik et al., 2001; Michalzik and Stadler, 2005). Higher soil temperatures may in turn enhance the leaching of DOM from organic soil layers (Andersson et al., 2000; Michalzik et al., 2001). In our study, this was only confirmed for DOC but not for DON, given the non-significant correlation between soil solution DON concentrations and soil temperature in the A horizon at the BRA site.

5.5   **Conclusions**

Following a sharp decline in atmospheric SO_4^{2-} and inorganic N depositions during the past two decades, forests in Flanders, the Northern part of Belgium, are under recovery from acidification. The concentrations and fluxes of DON in soil solution at five ICP Forests Level II plots showed increasing trends over a 9-year period starting in 2005. This mobilization of DON connects to the predominantly increasing trends of DOC levels observed in forest soils in the central parts of Europe and eastern US. The increase in DON in soil solution can be attributed to multiple interlinked abiotic processes, viz. increase in pH, decrease in soil solution Al^{3+} and SO_4^{2-} concentrations and ionic strength. But further in-depth statistical analysis able to cope with the multicollinearity among atmospheric deposition, soil solution, pH and DON level data will be needed. Such exercise requires long-term high-resolution datasets like the one presented here. Given the decrease in inorganic N deposition over the monitoring period, the generally decreasing trend in DOC:DON ratio in TF and soil solution does not appear to result from an altered N-balance. Also, no major shifts in air temperature were observed. We therefore argue that recovery from acidification may be the most plausible explanation for observed shifts in DON and DOC:DON trends over this 9-year period. Whether or not the

observed trends and patterns of DON also apply to a wider spatial scale will need to be further investigated, including its dependency on factors like latitude, level of N deposition, and hydrology.

5.6 **Appendix A**
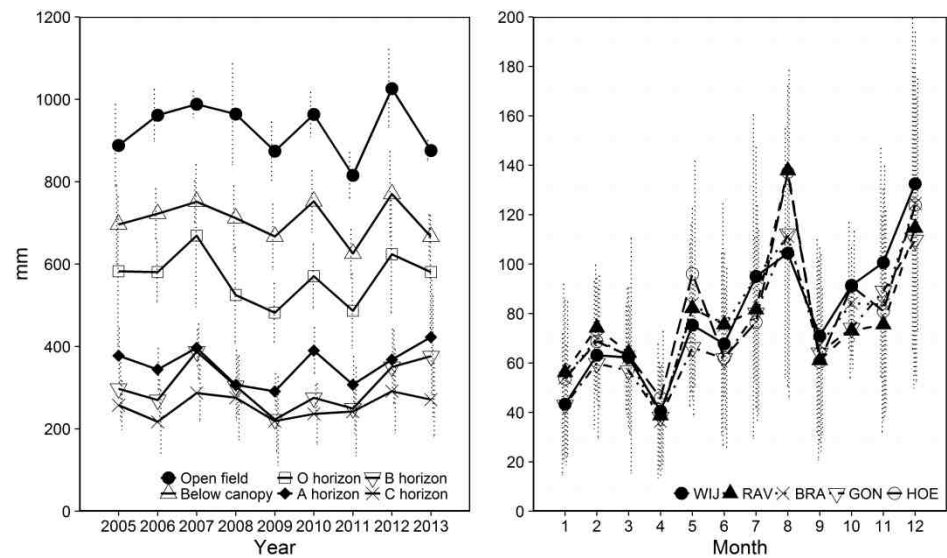
Figure 5.A1 Annual precipitation and drainage fluxes for the five plots (left) and mean monthly open field precipitation (mm) (2005–2013) with standard deviation (dashed bars). Data for 2005–2012 were taken from Verstraeten et al. (2014).

Figure 5.A2 Fortnightly DON concentration (mg L^{-1}) in deposition and soil solution, with trend lines (blue: linear regression line, red: LOESS curve).
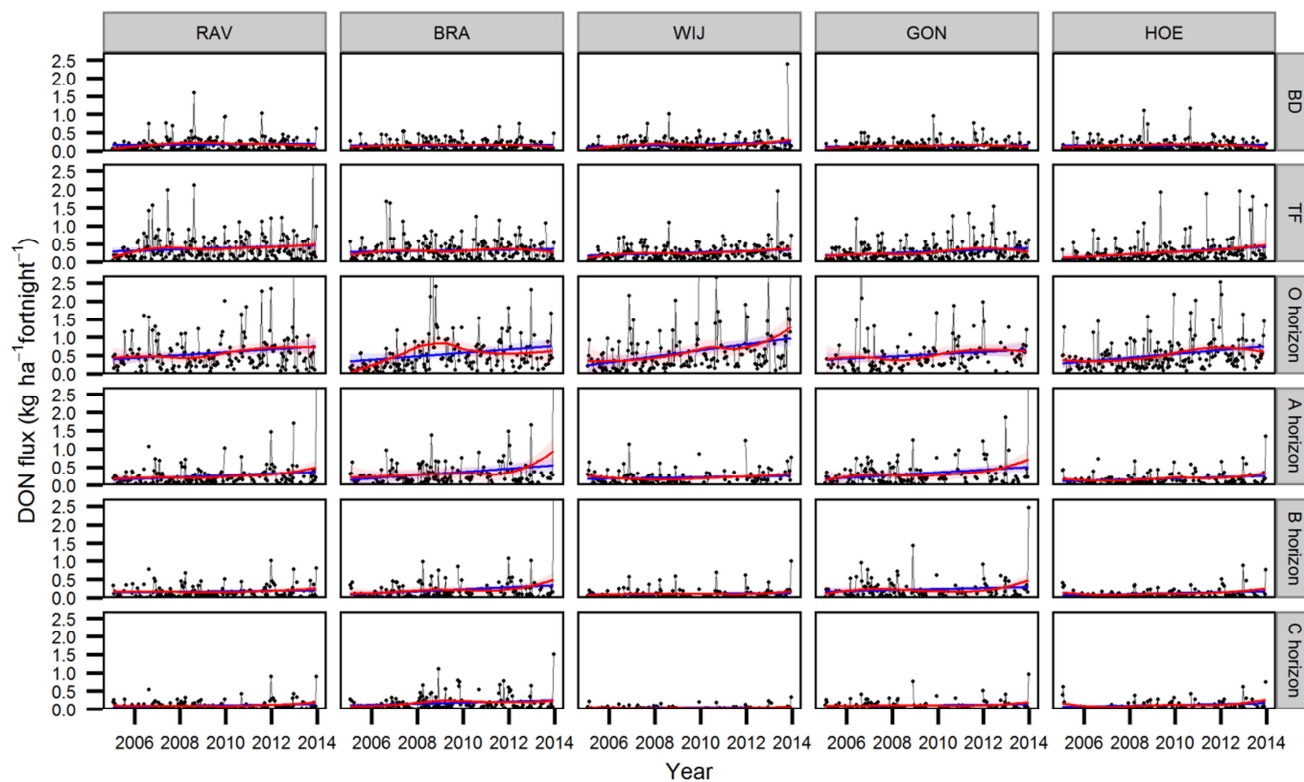
Figure 5.A3 Fortnightly DON flux (kg ha^{-1} fortnight^{-1}) in deposition and soil solution, with trend lines (blue: linear regression line, red: LOESS curve).
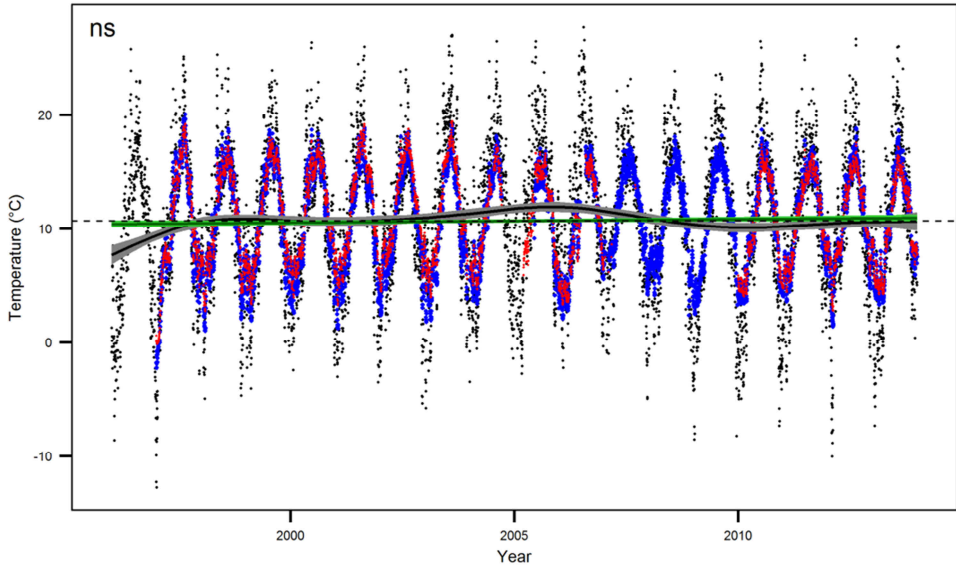
Figure 5.A4 Daily mean air temperature (black dots) and soil temperature in the A horizon (blue: 2 cm depth, red: 9 cm depth) at the BRA site (1996–2013). Dashed line: mean air temperature for the entire period (10.67 °C), solid green line: linear regression line for air temperature (with 95% confidence interval in light green), solid black line: gam model (air temperature ~ s(date, bc = "cs")) for air temperature (with 95% confidence interval in grey) and significance of Seasonal Mann-Kendall trends (ns: not significant).
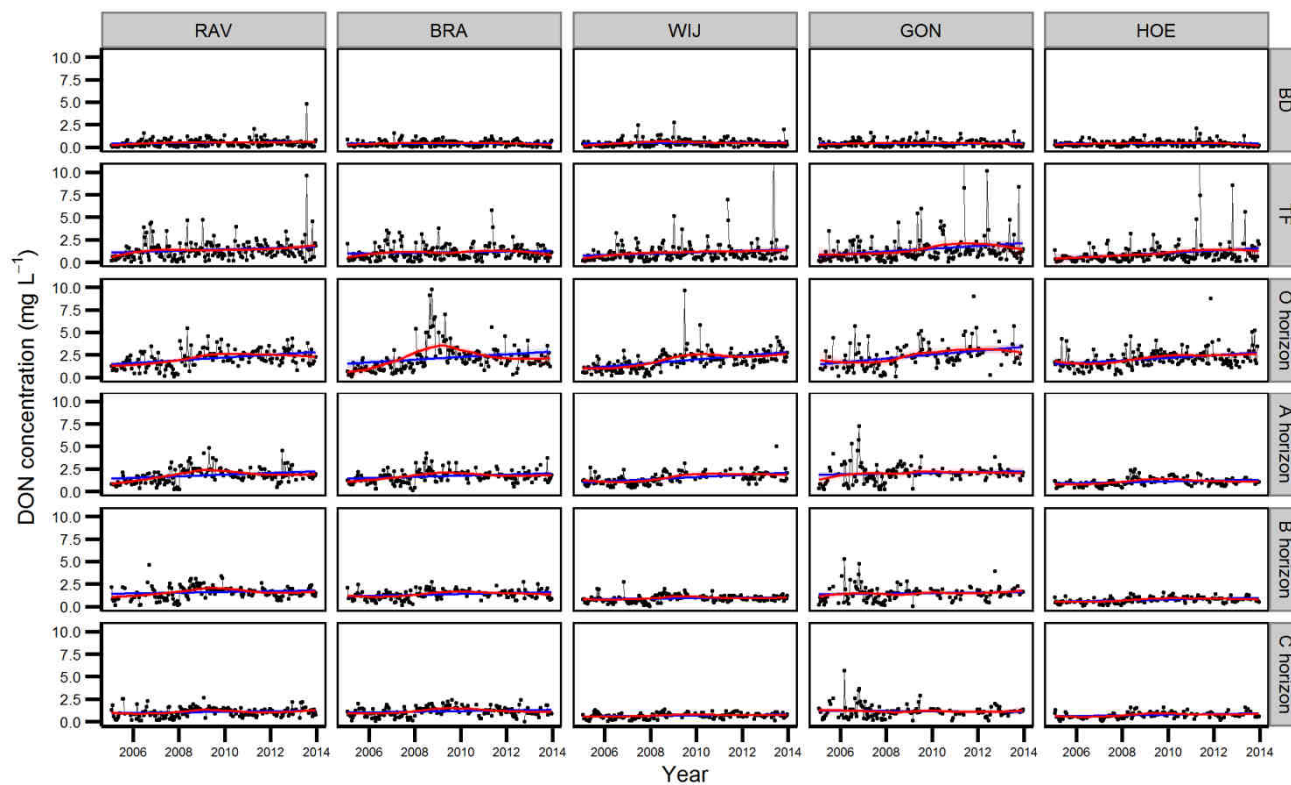
Figure 5.A5 Fortnightly DOC:DON ratio (molar) in deposition and soil solution, with trend lines (blue: linear regression line, red: LOESS curve).

Figure 5.A6 Soil solution pH (2005–2013) and significance of Seasonal Mann-Kendall trends (ns: not significant, (+): p < 0.1, +: p < 0.05, ++: p < 0.01, +++: p < 0.001), with trend lines (blue: linear regression line, red: LOESS curve).

Figure 5.A7 Fortnightly DOC concentration (mg L^{-1}) in deposition and soil solution, with trend lines (blue: linear regression line, red: LOESS curve).

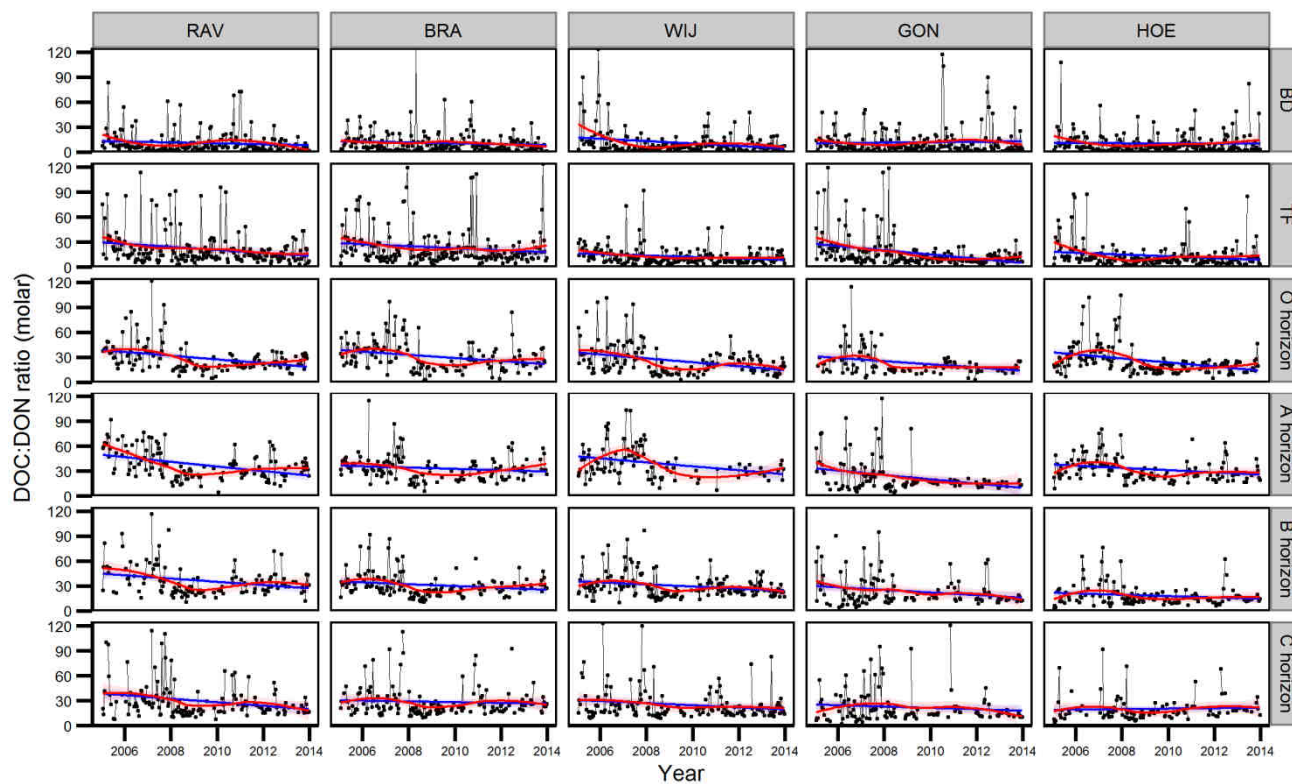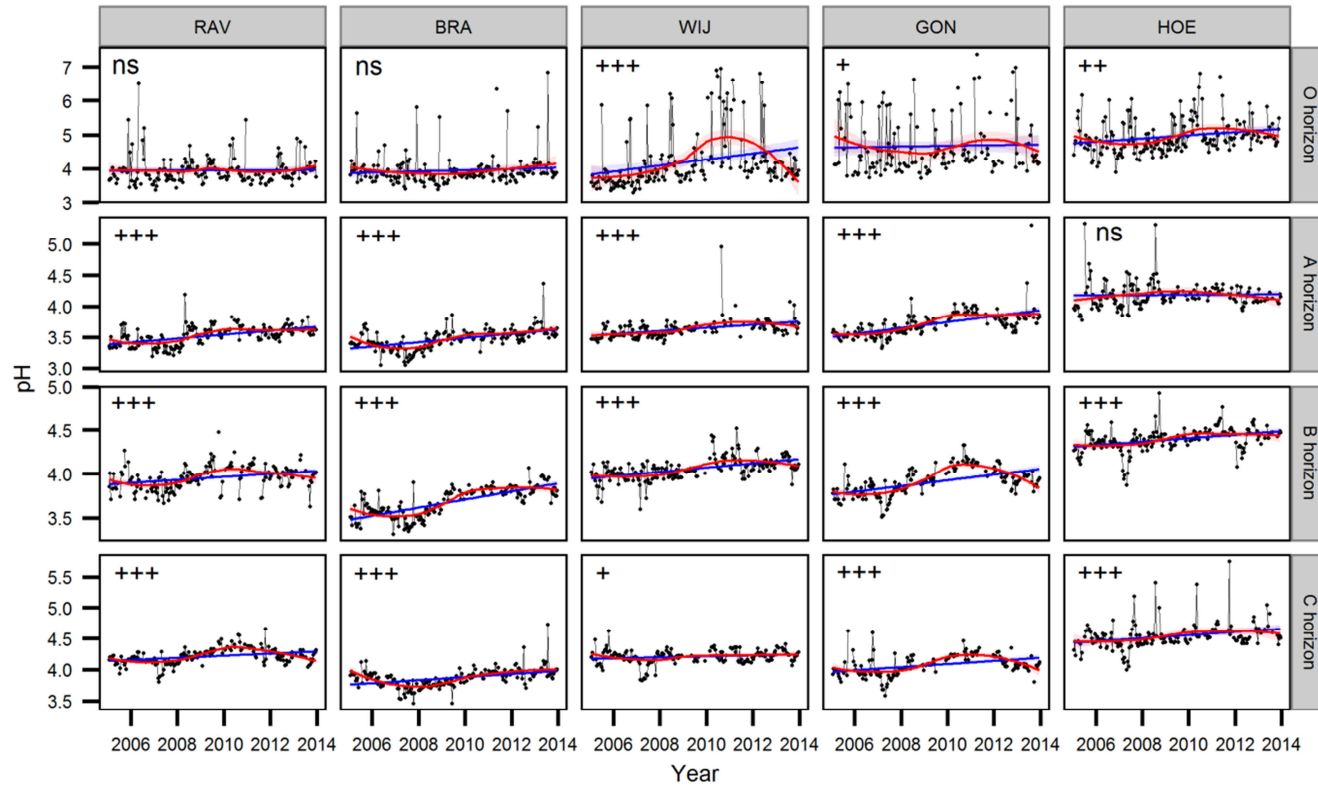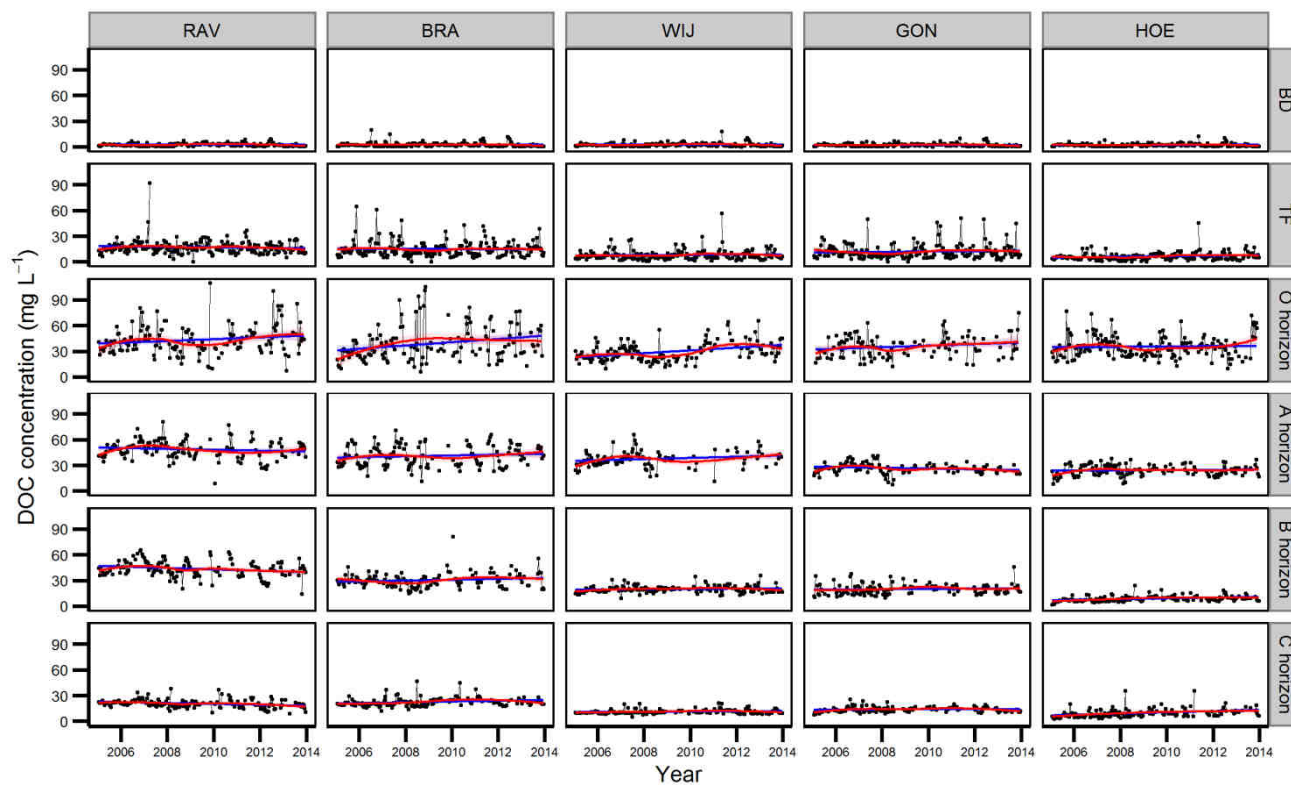# 6   MULTIPLE NITROGEN SATURATION INDICATORS YIELD CONTRADICTING CONCLUSIONS ON IMPROVING NITROGEN STATUS OF TEMPERATE FORESTS

Abstract

Nitrogen (N) depositions in Europe are decreasing, but this could not explain faster than expected improvement of N saturation indicators in temperate forests. Alongside there were local signs of initial recovery from acidification during the past three decades and enhanced leaching of dissolved organic carbon and nitrogen (DOC, DON). These two global change processes both affect total dissolved nitrogen (TDN) levels and often occur simultaneously, hence complicating mechanistic explanations for changing European forest N status. We aimed to test the hypothesis that forest N status in northwest Europe has started to improve. If this hypothesis is confirmed, we wanted to investigate to what extent such improvement is due to reduced N deposition. We evaluated the evolution of multiple N saturation indicators in five ICP Forests Level II plots in northern Belgium, using long-term soil solution and foliage datasets. The DON:TDN ratio (molar) in soil solution increased overall in the O horizon (mean 0.279–0.463, slope 0.023–0.037 yr^{-1}) and in the mineral soil (mean 0.134–0.78, slope 0.007–0.051 yr^{-1}) between 2005 and 2014. The DOC:NO_3^- ratio (molar) in soil solution increased in three plots in the O horizon (mean 6.84–22.15, slope 0.58–1.92 yr^{-1}) and in four plots in the mineral soil (mean 2.07–25.32, slope -0.06–5.76 yr^{-1}) between 2002 and 2014. The ratio of N and phosphorus (P) concentrations in foliage (mg g^{-1}) and the ratio of base cations (BC = Ca + K + Mg) and N concentrations in foliage (molar) remained unaltered between 1999 and 2013. Changes in the soil solution chemical composition thus confirmed an improvement in forest N status, despite sustained high NO_3^- concentrations, but biotic recovery appeared to be

lagging behind. This demonstrates that insight in forest recovery from N saturation requires a multiple indicator approach, and further monitoring of tree nutritional status alongside soil processes is needed to monitor the evolution of European forest N status.

6.1   **Introduction**

Atmospheric deposition of inorganic nitrogen (N) and sulphate (SO_4^{2-}) caused an accelerated acidification and N saturation of temperate forest soils and surface waters in large parts of Europe and the US mainly during the second half of the 20th century (van Breemen et al., 1984; Aber et al., 1989). In temperate forests, soil acidification often depleted base cations (calcium, potassium, magnesium), increased soil solution aluminium (Al^{3+}) concentrations and nitrate (NO_3^-) leaching, and disrupted dissolved organic matter cycling (Kalbitz et al., 2000; Aber et al., 2003; McDowell et al., 2004; Pregitzer et al., 2004; Monteith et al., 2007).

Despite a substantial decrease in inorganic N depositions in large regions of Europe during the past decade (Waldner et al., 2014), critical loads and limits, i.e. the level below which significant harmful effects do not occur according to present knowledge (Nilsson and Grennfelt, 1988) for inorganic N are still frequently exceeded in many European forests (Iost et al., 2012; Waldner et al., 2015). Despite publication of several papers on this matter it is still unclear how long N saturated forests will take to recover. Indeed, many factors, including management, SO_4^{2-} deposition and natural succession, change alongside inorganic N deposition, and individual compartments of the forest ecosystem (e.g. vegetation, below-ground communities, soil and soil solution) react with varying speed to changes in N availability (Stevens, 2016). Nitrogen availability also depends on forest size, forest type, soil type and sampling time and the complex interplay between biotic and abiotic processes (Pastor and Post, 1986; Callesen et al., 1999). In the present study we evaluate the evolution of forest N saturation in Flanders, a region in West-Europe where both inorganic N and SO_4^{2-} depositions strongly decreased, using a selection of indicators based on long-term data of the elemental concentrations in soil solution and tree mineral nutrition at intensive monitoring sites with varying soil types and tree species.

Long-term data on the concentrations of N species in soil solution collected at intensive forest monitoring plots yield crucial information about N availability and N saturation in forests. While unpolluted forests generally exhibit very limited N losses, consisting almost

entirely of dissolved organic nitrogen (DON), N saturated forests with low C:N ratio in organic layers typically show elevated NO_3^- leaching below the rooting zone (1989; Perakis and Hedin, 2002; Aber et al., 2003; Perakis and Sinkhorn, 2011). The ratio between DON and dissolved inorganic nitrogen (DIN) in soil solution, DON:DIN, has therefore been used as an indicator for N saturation in forests (Williams et al., 2001; 2004; Park and Matzner, 2006). Similarly, low ratios of DON to total dissolved nitrogen (TDN) in soil solution, DON:TDN, and of dissolved organic carbon (DOC) to NO_3^-, $DOC:NO_3^-$, are often used as indicators of soil N saturation (Currie et al., 1996; Sleutel et al., 2009; Taylor and Townsend, 2010).

The evaluation of forest N status may, however, be confounded when DOC and DON concentrations change alongside TDN and NO_3^- concentrations. Recovery from acidification was indeed found to mobilize DOC and DON (Verstraeten et al., 2016) in five ICP Forests Level II plots in northwest Europe. The concomitant evolutions in N deposition and recovery from acidification, both affecting DON mobility, therefore leads us to question the true share of reduced N depositions in a possible improving N status of these forests. The prime aim of this research was thus to assess recent evolutions in the N status of these five ICP Forests Level II plots in Flanders, northern Belgium. We monitored the concentrations of DON and TDN (2005–2014) in the deposition and soil solution and of DOC and NO_3^- (2002–2014) in the soil solution and critically assessed trends in classic molecular-ratio based indicators. Because throughfall DIN deposition in the plots decreased from 42.1 kg ha^{-1} yr^{-1} to 20.2 kg ha^{-1} yr^{-1} during the period 1994 to 2010 (Verstraeten et al., 2012), we hypothesized that the DON:TDN ratio (molar) and thus the $DOC:NO_3^-$ ratio (molar) increased over the past decade. We expect, however, that increased DON and DOC mobilization due to concomitant recovery from acidification renders these shifting ratios only partly indicative for the actual improvement in forest N status. Moreover, concentrations of DOC, DON, TDN and NO_3^- in throughfall and soil solution obviously are not representative of the tree biological status. Instead, the N status of forests can alternatively be derived from the foliar concentrations of N and phosphorus (P) and their ratio, N:P, in relation to tree species specific critical limits (Mellert and Göttlein, 2012; Veresoglou et al., 2014). A similar indicator is the ratio of the foliar concentrations of base cations (BC = Ca + K + Mg) and N, BC:N (Meesenburg et al., 2016). Tree nutritional status provides an integrative criterion for the assessment of site conditions and environmental factors (e.g. soil acidification, N saturation, climate change) and is important to control the success of restoration measures and to follow the

natural recovery of forest ecosystems from former anthropogenic impacts (Mellert and Göttlein, 2012). To more broadly track the impact of reduced N deposition on forest N status, we extended the evaluation with the 1999–2013 trends in the foliar N:P ratios and BC:N ratios and hypothesized that these had decreased and increased, respectively, as a consequence of lowered soil mineral N availability.

6.2   **Material and methods**

6.2.1   Study area

Five plots of the ICP Forests intensive monitoring network (Level II) in Flanders, northern Belgium, were included in this study. More details about these Level II plots are given in section 2.1.

6.2.2   Sample collection and measurements

Sampling of throughfall, stemflow and soil solution was carried out fortnightly from January 2005 till December 2014. A detailed description of the methods used for deposition sampling is given in section 2.2.1 and for soil solution sampling in section 2.2.2.

Sampling of fresh tree foliage was carried out biennially from 1999 till 2013 by professional tree climbers. A detailed description of the methods used for foliage sampling is given in section 2.2.3.

6.2.3   Chemical analysis

A description of the methods used for sample pre-treatment and for the determination of the concentrations (mg L^{-1}) of DOC, TKN, NH_4^+, NO_3^- and NO_2^- on the collected samples of throughfall, stemflow and soil solution is given in section 2.3.1. The methods used for the analysis of foliage samples are given in section 2.3.2.

6.2.4   Data handling

Concentrations of DOC and DON for 2005–2013 were taken from previous studies (Verstraeten et al., 2014; 2016), and were supplemented with new data for 2014. Concentrations of DON were calculated as TKN – NH_4^+. Concentrations of TDN were calculated as TKN + NO_3^- + NO_2^-. The ratio of DON and TDN concentrations (molar),

DON:TDN, and the ratio of DOC and NO_3^- concentrations (molar), DOC:NO_3^-, were calculated for each sample for which both concentrations were measured. Deposition fluxes of DIN (kg ha^{-1}) were calculated as the product of concentration (mg N L^{-1}) and the collected volume (L m^{-2}) of precipitation in the open field (BD) and below the canopy (throughfall + stemflow, further denoted as TF). The ratio of nitrogen to phosphorus concentration (mg g^{-1}) in foliage, N:P, and the ratio of base cations to nitrogen concentration (molar) in foliage, BC:N, were calculated for each foliage sample.

To determine the stage of N saturation in the plots based on the DON:TDN ratio we used critical limits as proposed by Williams et al. (2004) (stage 0: > 67% DON, stage 1: 33–67% DON, stage 2: < 33% DON). To check whether plots were N saturated based on the DOC:NO_3^- ratio we used the critical inflection point for soils (DOC:NO_3^- = 5.22) (Taylor and Townsend, 2010). Foliar nutritional status was judged by tree species specific critical limits for N and P concentrations and N:P ratios (van den Burg and Schaap, 1995; Mellert and Göttlein, 2012).

6.2.5   Statistical analysis

Data exploration and statistical analysis were performed in R version 3.3.0 (R Core Team, 2016). Since the data were not normally distributed (evaluated using the Shapiro-Wilk test included in the 'stats' package), the non-parametric Seasonal Mann-Kendall Test (Hirsch et al., 1982) included in the 'rkt' package (Marchetto, 2015) was used to detect monotonic trends in the DON:TDN ratio (2005–2014) and the DOC:NO_3^- ratio (2002–2014). The rate of annual change (increase or decrease) was expressed as a percentage in function of the Theil-Sen's slope (% yr^{-1}). Cross-site statistics (for inter-comparison of sites) were performed using the non-parametric Kruskalmc test (Multiple comparison test after Kruskal-Wallis test) included in the 'pgirmess' package (Giraudoux, 2015). Correlation between the fortnightly TF of DIN and the DON:TDN ratio and DOC:NO_3^- ratio in soil solution were evaluated using the Spearman's rank correlation test included in the 'stats' package. The nonparametric Mann-Kendall Test (Mann, 1945) included in the 'rkt' package (Marchetto, 2015) was applied to detect monotonic trends in the foliar concentrations and ratios, using the mean value for the five sampled trees in the same year.

6.3   **Results**

6.3.1   Trends in the DON:TDN ratio

The DON:TDN ratio in BD was comparable among plots (median 0.179–0.216) whereas there were small differences in this ratio in TF (median 0.202–0.261) (Table 6.1, Figure 6.1). In the O horizon (forest floor) the DON:TDN ratio was lowest in GON and WIJ (median respectively 0.279 and 0.306) and highest in BRA and HOE (median respectively 0.429 and 0.463). In the mineral soil (A, B, C horizons), the DON:TDN ratio was much lower in GON (median 0.134–0.147) compared to the other plots (median 0.290–0.780) and higher in HOE and WIJ than in RAV and BRA.

The DON:TDN ratio showed a limited general increase in BD (0.007–0.01 yr^{-1}) and a slightly stronger general increase in TF in the five forest plots (0.01–0.023 yr^{-1}) between 2005 and 2014 (Table 6.1, Figure 6.A1). In the soil solution, the DON:TDN ratio significantly increased with time at all depths. In the O horizon the smallest increase in the DON:TDN ratio was observed in GON (0.023 yr^{-1}) and the largest in HOE (0.037 yr^{-1}). In the mineral soil, the largest increase in the DON:TDN ratio was found in the two plots in coniferous forest (RAV and BRA) (0.028–0.051 yr^{-1}) and the smallest in GON (0.007–0.008 yr^{-1}). The annual rate of increase augmented from the A horizon (0.013–0.028 yr^{-1}) towards the C horizon (0.031–0.051 yr^{-1}) in all plots except the GON site, where it was constant with depth. In 2005 the 2nd critical limit for N saturation of Williams et al. (2004) was exceeded in all plots (N saturation stage 2: DON < 33% of TDN in soil solution) (Figure 6.1). The forest soil at the GON site remained N saturated during the 10-year period according to the criteria from Williams et al. (2004). The N status of the two plots in coniferous forest (RAV and BRA) improved from Williams et al. (2004)'s N saturation stage 2 to 1 (N saturation stage 1: DON 33–67% of TDN in soil solution). The N status in the WIJ site temporarily improved from stage 2 to 1 in the organic layer and from 2 to 0 (N saturation stage 0: DON > 67% of TDN in soil solution) in the mineral soil between 2005 and 2012, but fell back to stage 1 in 2013–2014. The N status in the HOE site improved from stage 2 to 1 in the B horizon and from stage 2 to 0 in the O, A and C horizon between 2005 and 2014.

In the O horizon, the DON:TDN ratio showed a strong negative correlation with the deposition of DIN in all plots (Figure 6.2). In the mineral soil the DON:TDN ratio was

negatively correlated with the deposition of DIN in RAV, HOE (A, B and C horizon) and BRA (B horizon).

Table 6.1 Median values and seasonal Mann-Kendall trends for the molar DON:TDN ratio (2005–2014) and the molar DOC:NO_3^- ratio (2002–2014), with the Theil-Sen's slope (annual change) and significance for the five locations (ns: not significant, (*): $p < 0.1$, *: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$). Different lowercase letters (a–d) denote plots with significantly different means between locations within groups/layers ($p < 0.05$).

Plot	Sampli Depth (cm)	DON:TDN (molar)		DOC:NO_3^- (molar)	
		Median (–)	Slope	Median (–)	Slope
BD					
RAV		0.188a	0.008**		
BRA		0.191a	0.007(*)		
WIJ		0.216a	0.008*		
GON		0.179a	0.009**		
HOE		0.210a	0.010*		
TF					
RAV		0.218ab	0.013***		
BRA		0.202a	0.010***		
WIJ		0.214ab	0.010**		
GON		0.240bc	0.017***		
HOE		0.261c	0.023***		
O horizon					
RAV		0.377b	0.033***	15.54b	1.63***
BRA		0.429c	0.028***	22.15c	ns
WIJ		0.306a	0.027***	6.84a	0.58***
GON		0.279a	0.023***	8.48a	ns
HOE		0.463c	0.037***	17.35b	1.92***
A horizon					
RAV	10–25	0.346b	0.028***	10.72b	1.16***
BRA	15–25	0.372b	0.028***	14.18bc	1.64***
WIJ	10–20	0.564c	0.023***	21.27c	3.83***
GON	10–20	0.147a	0.007**	2.73a	-0.06(*)
HOE	10–15	0.746c	0.013***	25.32c	4.49***
B horizon					
RAV	30–45	0.349b	0.042***	12.03c	1.81***
BRA	30–55	0.343b	0.037***	10.16c	1.93***
WIJ	45–70	0.447c	0.030***	14.59c	2.09***
GON	25–40	0.134a	0.008**	2.55a	ns
HOE	20–30	0.396bc	0.020***	6.41b	0.47***
C horizon					
RAV	70–95	0.325b	0.051***	9.52b	1.91***
BRA	70–90	0.290b	0.045***	7.05b	1.40***
WIJ	75–110	0.428c	0.031***	11.61bc	2.43***
GON	45–55	0.135a	0.007*	2.07a	ns
HOE	35–55	0.780d	0.032***	17.12c	5.76***
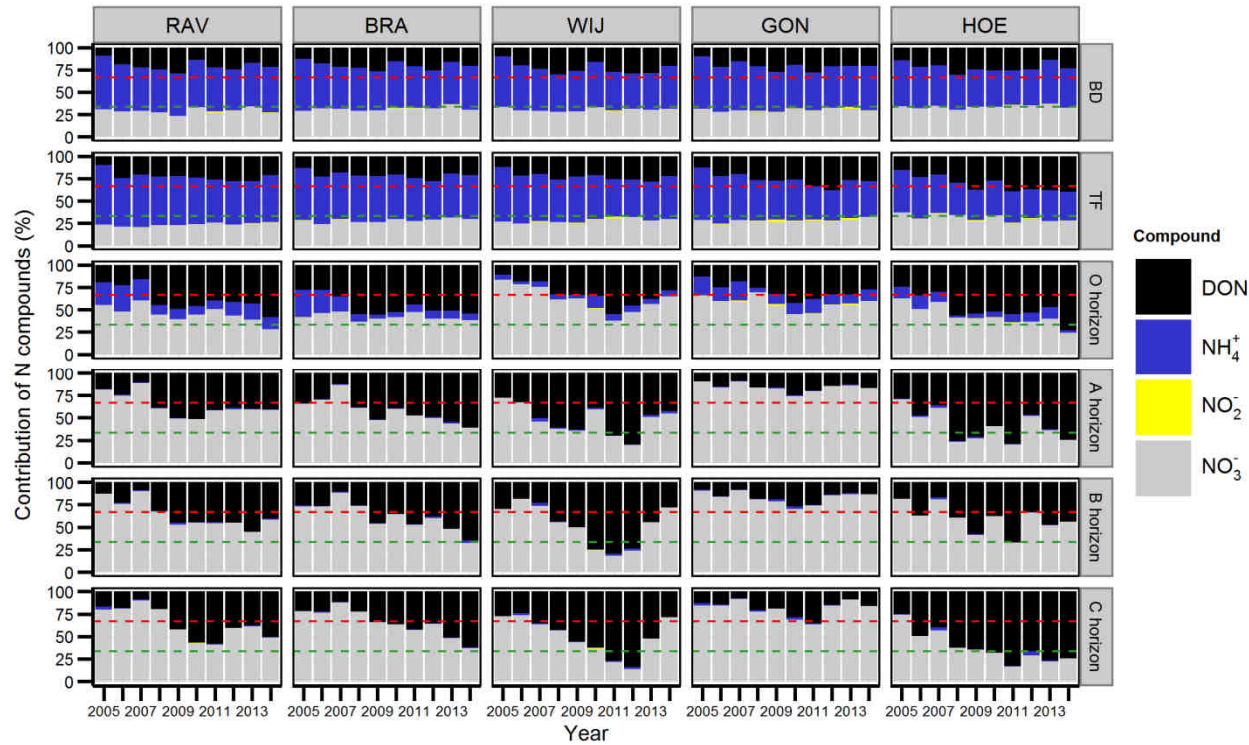
Figure 6.1 Annual contribution (%) of N compounds in deposition and soil solution for the five locations with Williams et al. (2004)'s critical limits for stages of N saturation (0: > 67% DON indicated by the green dashed line, 1: 33–67% DON, 2: < 33% DON indicated by the red dashed line).

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Figure 6.2 Soil solution DON:TDN ratio in function of TF DIN deposition (2005–2014) for the five locations with significance of the correlation (ns: not significant, (-): $p < 0.1$, -: $p < 0.05$, --: $p < 0.01$, ---: $p < 0.001$), Williams et al. (2004)'s critical limits for stages of N saturation (0: DON:TDN > 0.67 indicated by the green dashed line, 1: 0.33 < DON:TDN < 0.67, 2: DON:TDN < 0.33 indicated by the red dashed line), and trend lines (blue solid line: linear regression line, red solid line: LOESS curve) with 95% confidence intervals (light blue: linear regression, light red: LOESS curve LOESS curve). The LOESS curve (locally weighted polynomial regression) shows that the relationship is often close to linear in the range with sufficient data.

6.3.2   Trends and patterns of the DOC:NO$_3^-$ ratio

The concentrations of DOC and NO$_3^-$ in soil solution were negatively correlated at all depths in WIJ and HOE, in the mineral soil in BRA and in the A horizon in RAV (Figure 6.A2). In the O horizon the DOC:NO$_3^-$ ratio was markedly lower in WIJ and GON (median respectively 6.84 and 8.48) compared to the other three plots (median 15.54–22.15) (Table 6.1). The DOC:NO$_3^-$ ratio in the O horizon significantly increased in RAV, WIJ and HOE and remained unchanged in BRA and GON between 2002 and 2014 (Table 6.1, Figure 6.3, Figure 6.A3). In 2002, the DOC:NO$_3^-$ ratio was still frequently below the critical inflection point for N saturation (DOC:NO$_3^-$ = 5.22) in the O horizon in all plots except the BRA site, while in 2014 the critical limit was respected in BRA, RAV and HOE (Figure 6.3).

In the mineral soil, the DOC:NO$_3^-$ ratio was significantly lower in GON (median 2.07–2.73) compared to the other plots (median 6.41–25.32) (Table 6.1). The DOC:NO$_3^-$ ratio in the mineral soil increased significantly with time in the A, B and C horizon in all plots except GON, where it remained stable (B and C horizon) or even slightly decreased (A horizon). In 2002, the critical inflection point for N saturation was permanently surpassed in the mineral soil in all plots, while in 2014 this was still often the case in WIJ and GON but no longer in RAV, BRA and HOE (Figure 6.3).

In RAV, BRA and WIJ, the DOC:NO$_3^-$ ratio showed a negative correlation with the deposition of DIN (Figure 6.4). In GON and HOE we found no consistent relationship between the DOC:NO$_3^-$ ratio and the deposition of DIN.
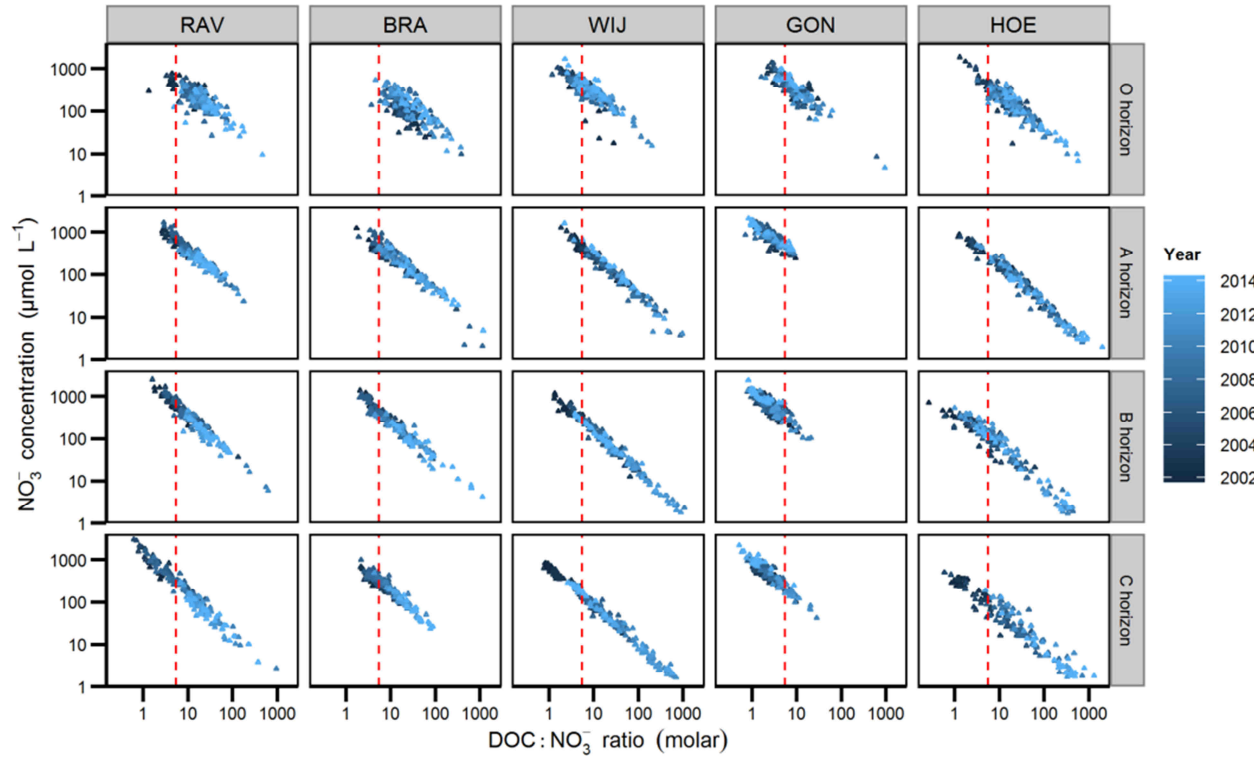
Figure 6.3 Soil solution NO_3^- concentration in function of the $DOC:NO_3^-$ ratio (2002–2014) for the five locations and critical inflection point for soils ($DOC:NO_3^- = 5.22$) as proposed by Taylor and Townsend (2010) indicated by the red dashed line. The $DOC:NO_3^-$ ratio should be above the critical inflection point.
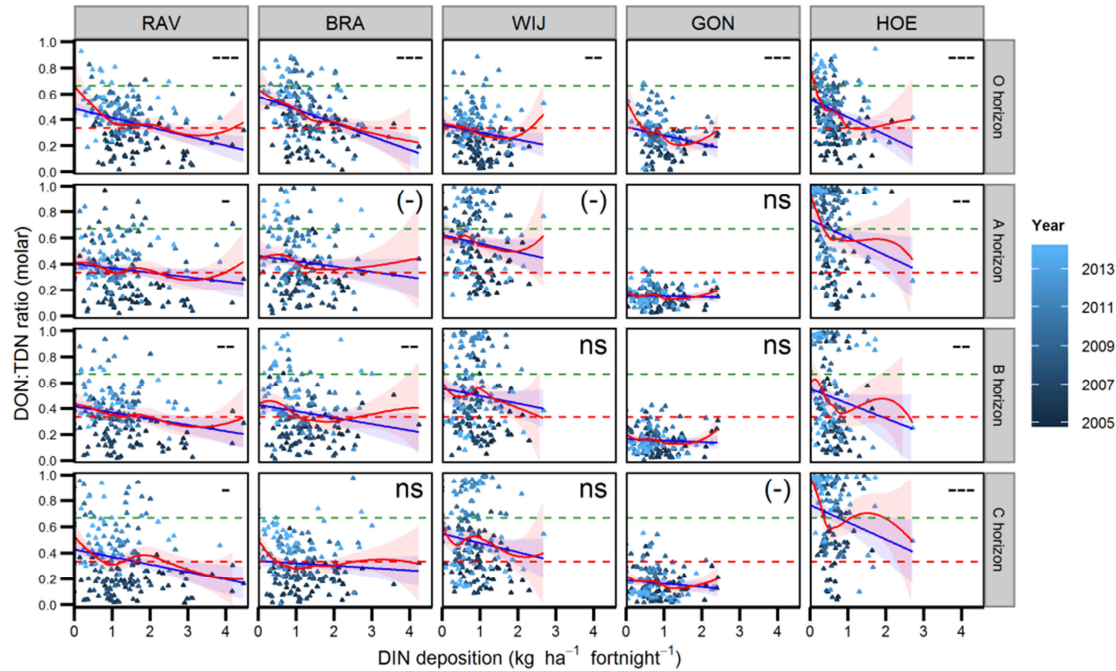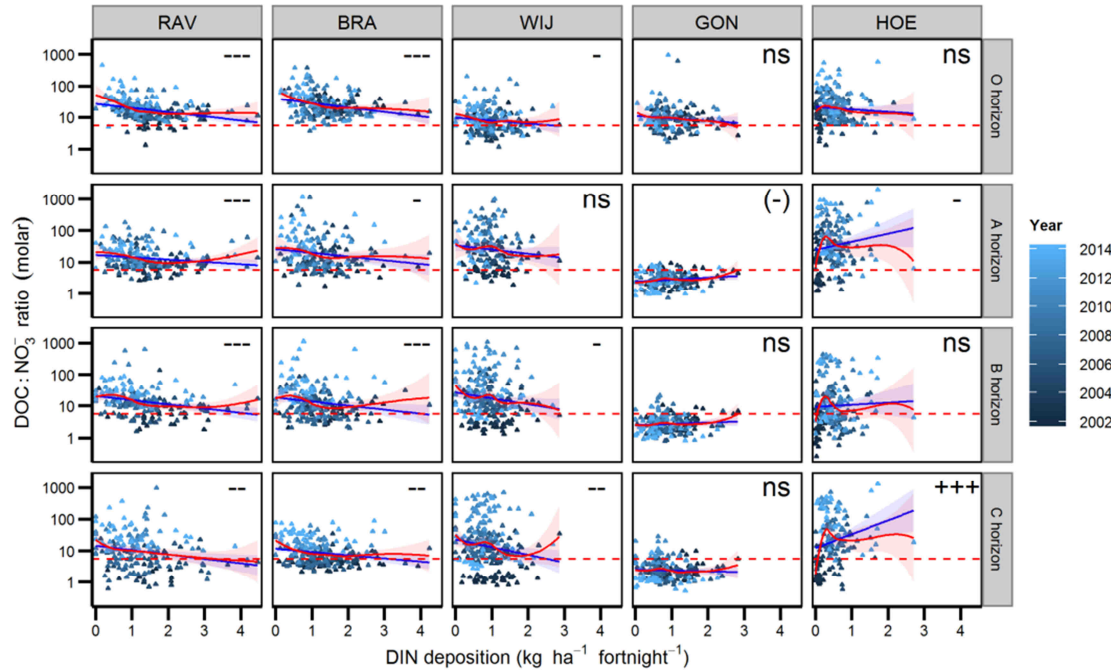
Figure 6.4 Soil solution DOC:NO_3^- ratio in function of TF DIN deposition (2002–2014) for the five locations with significance of the correlation (ns: not significant, (-): $p < 0.1$, -: $p < 0.05$, --: $p < 0.01$, --- or +++: $p < 0.001$), critical inflection point for soils (DOC:NO_3^- = 5.22) as proposed by Taylor and Townsend (2010) indicated by the red dashed line, and trend lines (blue solid line: linear regression line, red solid line: LOESS curve) with 95% confidence intervals (light blue: linear regression, light red: LOESS curve LOESS curve). The LOESS curve (locally weighted polynomial regression) shows that the relationship is often close to linear in the range with sufficient data. The DOC:NO_3^- ratio should be above the critical inflection point.

6.3.3   Trends in tree mineral nutrition

The mean foliar N concentration (Table 6.2) was constantly above the upper limit in all plots, indicating luxury consumption of N by the trees (Figure 6.A4). The foliar N concentration decreased in the BRA site ($p < 0.05$) and remained unchanged in the other plots between 1999 and 2013. The mean foliar P concentration was in the normal range in all plots, but on the lower side of this range in BRA, WIJ and GON (Figure 6.A5). The foliar P concentration remained unchanged in the plots between 1999 and 2013. The foliar concentration of Ca, K and Mg remained unchanged between 1999 and 2013 (data not shown), except for an increase in the foliar concentration of Ca in WIJ ($p < 0.01$).

The mean foliar N:P ratio of current year needles was above the upper critical limit (unbalanced nutrition) both for Scots pine *Pinus sylvestris* L. (14.1) in BRA (15.37) between 1999 and 2013 (Figure 6.5) and for Corsican pine *Pinus nigra* ssp. *laricio* var. *Corsicana* Loud. (12) in RAV (14.85). The mean foliar N:P ratio of common oak *Quercus robur* L. leaves was in the normal range (balanced nutrition, 9.3–19.6) in GON (18.45), and for European beech *Fagus sylvatica* L. leaves (10–18.9) in HOE (16.34). It was above the upper critical limit in WIJ (19.65). Both the mean foliar N:P ratio and BC:N ratio did not change in the plots between 1999 and 2013 (Figure 6.6).

Table 6.2 Mean foliar concentrations of N, P and base cations (mg g^{-1} dry weight at 105 °C) for leaves and current year needles in the five Level II plots in Flanders (1999–2013).

Plot	Tree species	N (mg g^{-1})	P (mg g^{-1})	Ca (mg g^{-1})	K (mg g^{-1})	Mg (mg g^{-1})
Coniferous forests						
RAV	*Pinus nigra* ssp. *laricio*	20.5	1.40	1.68	7.41	0.73
BRA	*Pinus sylvestris* L.	22.1	1.45	2.81	6.84	0.87
Deciduous forests						
WIJ	*Fagus sylvatica* L.	26.4	1.35	4.02	10.39	0.87
GON	*Quercus robur* L.	27.8	1.53	7.34	11.83	1.71
HOE	*Fagus sylvatica* L.	24.1	1.49	8.86	8.93	1.27
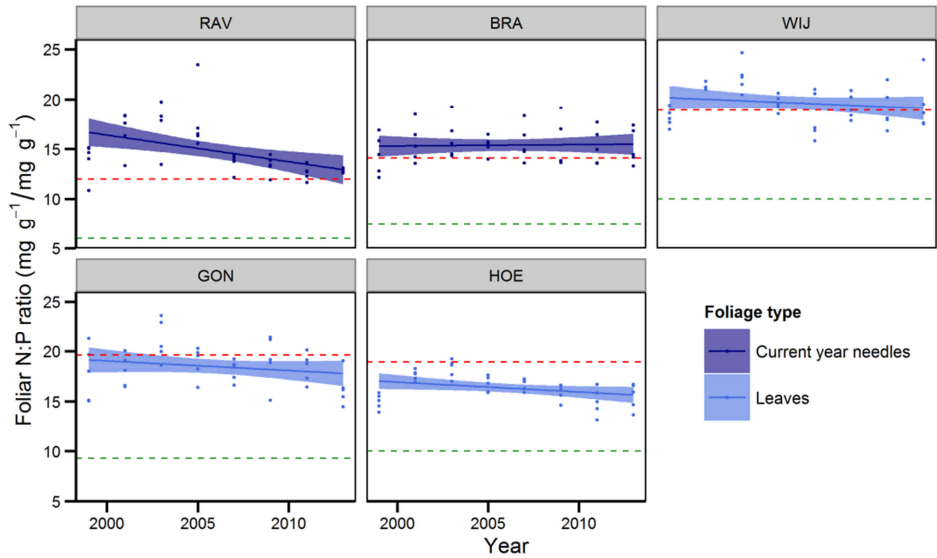
Figure 6.5 Foliar N:P ratio (1999–2013) for the five locations with critical lower limit (green dashed line) and upper limit (red dashed line) (van den Burg and Schaap, 1995; Mellert and Göttlein, 2012). Coloured zones represent the 95% confidence interval. Trends were not significant.
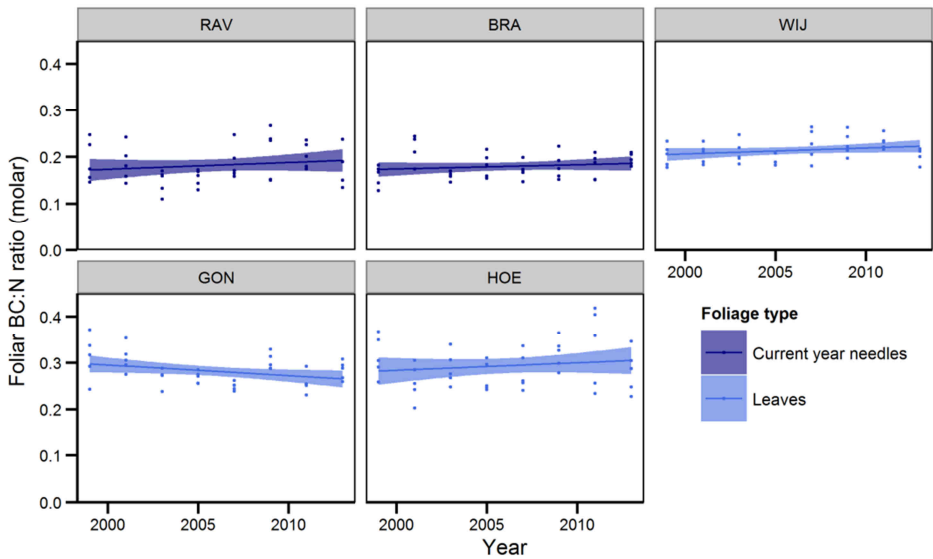

Figure 6.6 Foliar BC:N ratio (1999–2013) for the five locations. Coloured zones represent the 95% confidence interval. Trends were not significant.

6.4   **Discussion**

6.4.1   Nitrogen status based on soil solution chemistry

Trend analysis demonstrated an increase in the soil solution DON:TDN ratio in the five studied Level II plots between 2005 and 2014. In parallel, the soil solution DOC:NO_3^- ratio increased in the RAV, BRA, WIJ and HOE plots between 2002 and 2014. This confirms our hypothesis that these N saturated forest ecosystems are evolving, to a variable extent, towards abiotic conditions typical for unpolluted forest ecosystems (Aber et al., 1989; Perakis and Hedin, 2002; Perakis and Sinkhorn, 2011). The lack of recovery from N saturation at the GON site could likely be explained by the higher clay content of that soil (Verstraeten et al., 2016), with a 4–10 times higher cation exchange capacity (CEC) compared to the other (coarser textured) soils, and therefore also higher N retention capacity, and N availability and NO_3^- concentrations in soil solution (Pastor and Post, 1986; Callesen et al., 1999). The soil C:N ratio at 20–40 cm and 40–80 cm depth were indeed only 12.0 and 7.8, respectively (Verstraeten et al., 2012), and lower than in the RAV, BRA and WIJ plots. At the same time, the presence of a clay lens at 40–80 cm depth at GON (Verstraeten et al., 2016), must have restricted vertical water fluxes and therefore NO_3^- leaching, leading to generally lower DOC:NO_3^- ratios. These results suggest that finer textured soils recover more slowly from N saturation, possibly due to their stronger capacity to retain DON and NH_4^+ and limited leaching of excess NO_3^-, but this would need to be confirmed on a larger set of soils.

It is difficult to frame our results within a European context, because unfortunately Europe-wide studies on recent evolutions in the N status of temperate forests are lacking (Stevens, 2016). Trends reported by local or regional studies using long-term data from intensive forest monitoring plots are inconsistent, varying between a tendency towards recovery from N saturation in the Czech Republic (Oulehle et al., 2011), mixed trends in the UK depending on the level of DIN deposition (Vanguelova et al., 2010) and increasing N saturation in the Belgian Ardennes (Jonard et al., 2012) and in Solling, Germany (Meesenburg et al., 2016). These inconsistent varying results could be explained by regional differences in the evolution of S and inorganic N depositions, driven by industrial and agricultural development, and by local differences in the strength of sinks (vegetation, soil) and N cycling processes, which determine how N saturation is manifested in the ecosystem (Lovett and Goodale, 2011; Niu et al., 2016).

The two most obvious drivers for the tendency towards recovery from N saturation in the five studied forests are the relatively fast decrease in both acidifying and eutrophying depositions in the past two decades. Throughfall depositions of DIN decreased by 2.4–5.0% yr^{-1} in these plots between 1994 and 2010, which can be explained by a substantial reduction of NH_3 emissions mainly by the agricultural sector (particularly the large scale adoption of low-NH_3-emission stables, soil-injection of animal slurry and a slight decrease in livestock numbers) but also by decreased co-deposition with SO_4^{2-} (Verstraeten et al., 2012; VMM, 2016a). The study area (Flanders) is thus among the regions in Europe where DIN depositions decreased more than the European average of 1.3–1.8% yr^{-1} between 2000 and 2010 (Waldner et al., 2014). Soil solution NO_3^- and DON are often positively and negatively correlated, respectively, with the TF of DIN (Perakis and Hedin, 2002; Park and Matzner, 2006). The predominantly negative correlation that we observed between the TF of DIN and the DON:TDN ratio (Figure 6.2) and DOC:NO_3^- ratio (Figure 6.4) in soil solution would thus confirm that the decrease in the TF of DIN contributed to higher ratios, suggesting a possible improvement of the N status in the plots. This was also supported by the increasing DON:TDN ratio in BD and TF (Table 6.1). However, NO_3^- leaching in the plots decreased faster than could be expected from the annual decrease in the TF of DIN, which still exceeded considerably the critical load of 10 kg N ha^{-1} yr^{-1} above which European temperate forests are susceptible to elevated NO_3^- leaching (Dise and Wright, 1995; Verstraeten et al., 2012). This is in line with the faster than expected decline of NO_3^- leaching observed at three intensive forest monitoring plots receiving high DIN depositions in the Czech Republic and the UK (Vanguelova et al., 2010; Oulehle et al., 2011).

The decrease in DIN depositions alone could not fully explain the initial recovery from N saturation in the Flemish Level II plots. Simultaneously with the deposition of DIN the deposition of SO_4^{2-} sharply decreased in the Flemish Level II plots, by 4.2–7.5% yr^{-1} between 1994 and 2010 (Verstraeten et al., 2012), which is comparable to the European average of 6% yr^{-1} between 2000 and 2010 (Waldner et al., 2014). Oulehle et al. (2011) identified the strong decrease in SO_4^{2-} depositions, and subsequent recovery from acidification, as the main driver for the fast decrease in NO_3^- leaching at a highly acidified spruce forest in the Czech Republic. Recovery from acidification is manifested by increasing pH and decreasing Al^{3+} concentrations in soil solution (Vanguelova et al., 2010; Oulehle et al., 2011; Verstraeten et al., 2012). The latter is expected to reduce the formation of organo-metal complexes and increase the solubility of organic matter, which

could partly explain the predominantly increasing trends of DOC and DON concentrations in the soil solution of forests and connected surface waters (de Wit et al., 2007; Monteith et al., 2007; Scheel et al., 2007). Also in the Flemish Level II plots the increasing DON:TDN ratio and DOC:NO_3^- ratio are probably closely linked to recovery from acidification, given the fact that soil solution Al^{3+} concentrations strongly decreased, soil solution DOC and DON concentrations both increased and soil solution pH in the mineral soil increased by about 0.5 units between 2005 and 2013 (Verstraeten et al., 2012; 2014; 2016). Verstraeten et al. (2016) furthermore explained increased mobilization of DOC and DON by lowered ionic strength as a result of decreasing temporal trends in soil solution Al^{3+} and SO_4^{2-}, both linked to diminishing acid deposition in these five Level II plots. Lastly, in well-oxygenated environments like the rooting zone in forests on well-drained soils the increase in DOC concentrations under recovery from acidification is also expected to stimulate the activity of heterotrophic bacteria in the mineral soil by alleviating the C limitation. When resource C:N ratios match the stoichiometric demands of microbial anabolism, heterotrophic microbes maintain low NO_3^- concentrations through intensified N turnover and retention of incoming N from the organic layer (Taylor and Townsend, 2010; Helton et al., 2015). The increasing trends of the DOC:NO_3^- ratio that we observed in four plots could indicate that recovery from N saturation is not necessarily limited to abiotic conditions, but could also involve initial recovery of soil microbial communities. A strong microbial recovery at the plots in Flanders seems unlikely though, considering the very low pH-$CaCl_2$ of about 3–4 in the mineral soil.

The fast response of the DOC:NO_3^- ratio and DON:TDN ratio in soil solution to changing environmental conditions makes them suitable indicators for early detection of shifts in forest N status. However, it should be noted that the critical limit for the molar DOC:NO_3^- ratio proposed by Taylor and Townsend (2010) for soils (5.22) coincided with soil solution NO_3^- concentrations ranging between 100 and 1000 µmol L^{-1} (1.4–14 mg N L^{-1}) (Figure 6.3). Compared with the critical limits for N concentration in soil solution published in Waldner et al. (2015) and adopted from Iost et al. (2012) (0.2–0.4 mg N L^{-1} in the O horizon, 1 mg N L^{-1} in the mineral soil) NO_3^- concentrations were still elevated, although the critical limit for DOC:NO_3^- in our plots was respected. This raises the question whether the critical limit of Taylor and Townsend (2010) is stringent enough for European forest soils. Taylor and Townsend (2010) derived their critical limit from an exponential model based on data from 100 soils mostly located in the USA, including a mixture of different soil types (wetlands, moorlands, temperate deciduous and coniferous forests

along a longitudinal and altitudinal gradient). Further research is needed to check whether the results of our study could be generalized and whether the critical DOC:NO$_3^-$ limit should be adjusted for European temperate forest soils.

6.4.2   Nitrogen status based on tree mineral nutrition status

The foliar N:P ratio and BC:N ratio remained unchanged in the Flemish Level II plots between 1999 and 2013. Foliar N concentrations also remained near or above the critical limits determined by Mellert and Göttlein (2012), indicating luxury consumption of N by the trees, while P nutrition generally was in the lower part of the normal range, and tending towards latent deficiency at the BRA site. Consequently, tree nutritional status does not confirm our hypothesis that these temperate forests are under recovery from N saturation, but rather points to a nearly stable but unbalanced mineral nutrition. For common oak (*Quercus robur* L.), Jonard et al. (2015) also reported a stable tree nutrient status for Level II plots across Europe, but the mean foliar N:P ratio in GON (18.45) was higher, and thus less balanced, than the European mean (16.35). The stable trends that we observed for European beech (*Fagus sylvatica* L). and Scots pine (*Pinus sylvestris* L). were in line with parallel long-term trends for tree defoliation observed in the plots of the ICP Forests large-scale forest condition monitoring network (Level I) in Flanders (Cools et al., 2016) but contrasted with the predominantly increasing trends of the foliar N:P ratio in Level II plots across Europe, which indicated a deterioration of tree mineral nutrition at the European scale (Jonard et al., 2015). For Scots pine, this could be explained by the fact that the foliar N:P ratio in current year needles in BRA (15.37) was already much higher, and thus less favourable, than the European mean (11.09). On the other hand, for European beech, the mean foliar N:P ratio in HOE (16.34) and WIJ (19.65) was lower than the European mean (20.31), suggesting that the phosphorus nutrition of beech forests in Flanders is slightly better than the European mean. The stable foliar BC:N ratios that we observed are in line with stable N:Mg and N:K ratios observed for common oak, European beech and Scots pine at the European scale (Jonard et al., 2015).

A discrepancy between the evolution in soil N status and the response at plant level was also found by Jonard et al. (2012), who observed increasing NO$_3^-$ concentrations in soil solution and stable foliar N content. The explanation why tree nutritional status did not respond yet to the recovery from N saturation indicated by changes in the soil solution chemical composition in the five studied forests could possibly be found in the N saturation hypothesis (Aber et al., 1989; Aber et al., 1998; Galloway et al., 2003). Nitrate

leaching is negligible in the early stages of N saturation, but increases exponentially in the late stage of N saturation. According to the N saturation hypothesis revised by Galloway et al. (2003) foliar N concentration is expected to increase linearly in the early stages of N saturation and to slightly decrease during the late stage of N saturation. Therefore, it is to be expected that strong reductions in NO_3^- leaching during the initial phase of recovery from N saturation will not yet result in significant changes in the foliar N content. It is impossible to predict future timing for normalization of foliar N:P ratios because of two main reasons. Firstly, on-going soil pH increases are still in the Al buffer range (pH 4.0 for gibbsite). Further rises in pH and lowering of ionic strength could then both abruptly lower soil solution levels of Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ with possible positive effects on P availability as well (Kochian et al., 2004). Secondly, at the currently very low soil pH in all studied soils, bacterial activity must be minimal, but could also increase non-linearly when pH-inflection points are reached. If so, NO_3^- levels may increase again due to microbial decomposition of native soil organic matter (Aber et al., 1989), while DOC and DON levels would change in unpredictable directions alongside. Continued monitoring is needed to confirm whether there exists a time lag between chemical and biological restoration.

As explained in a review by Stevens (2016) the response time of ecosystem compartments to changes in inorganic N depositions can vary greatly among ecosystem compartments. Soil solution NO_3^- and NH_4^+ concentrations can recover relatively rapidly, but this could take many years or even decades for vegetation species composition, tree mineral nutrition, below-ground communities and soil processes (Meesenburg et al., 2016; Stevens, 2016). It is thus not possible to evaluate ecosystem N status correctly based on a single type of indicator only, leading us to the key message of our study: recovery from N saturation in forests should be evaluated using a multiple indicator approach, with a selection of indicators that provide information about the different ecosystem compartments (e.g. soil solution chemistry, foliar chemistry, ground vegetation, mineralisation, N stocks).

6.5   **Appendix A**
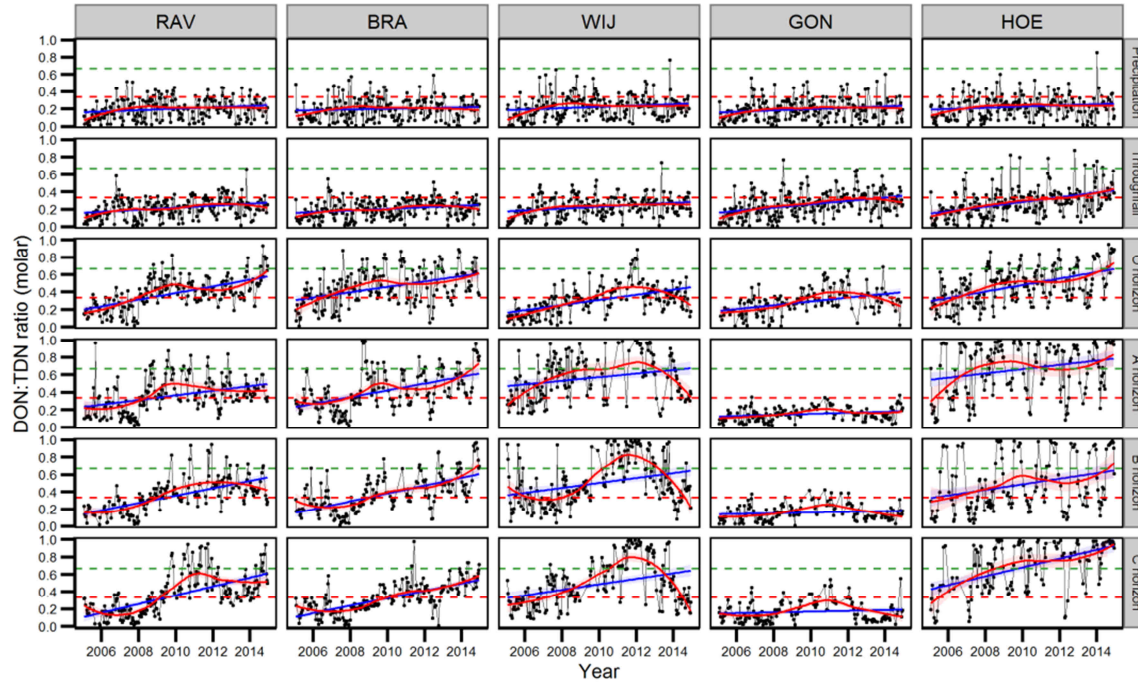
Figure 6.A1 Fortnightly DON:TDN ratio in deposition and soil solution for the five locations, with Williams et al. (2004)'s critical limits for stages of N saturation (0: DON:TDN > 0.67 indicated by the green dashed line, 1: 0.33 < DON:TDN < 0.67, 2: DON:TDN < 0.33 indicated by the red dashed line) and trend lines (blue: linear regression line, red: LOESS curve).
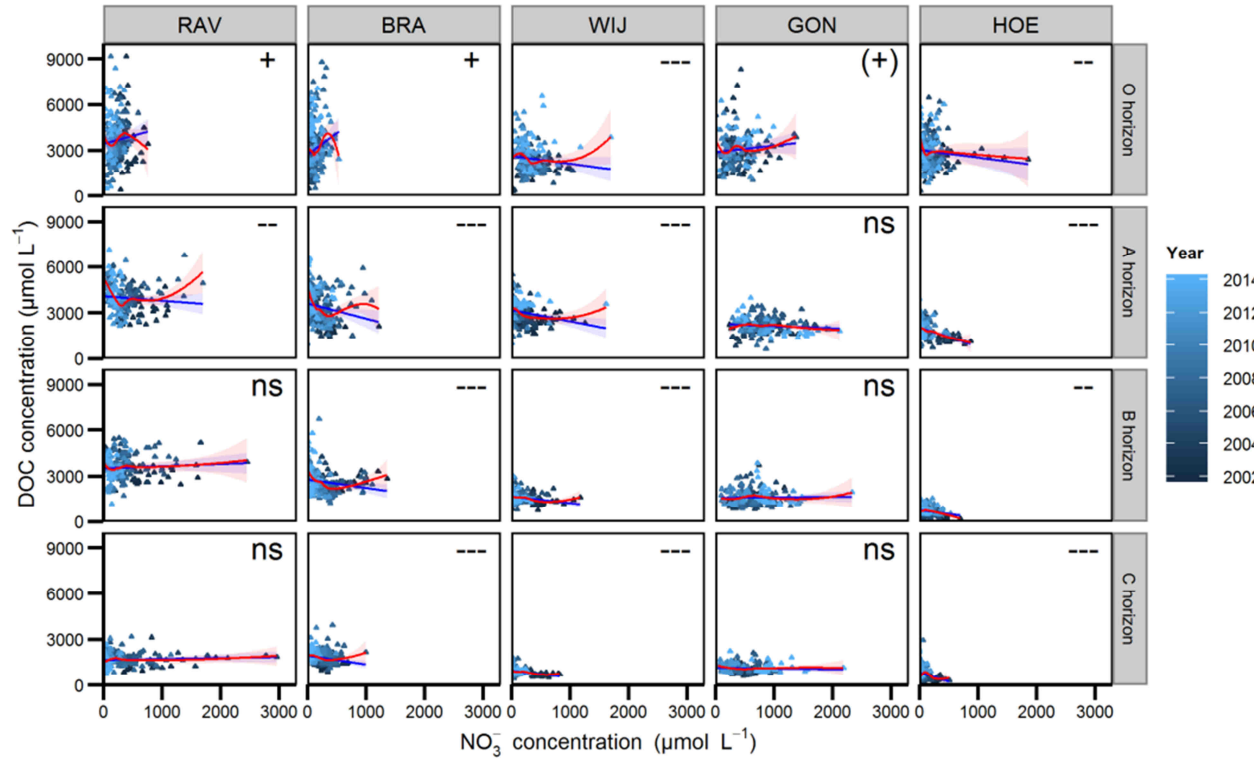
Figure 6.A2 Soil solution DOC concentration in function of NO₃⁻ concentration for the five locations (2002–2014) with trend lines (blue: linear regression line, red: LOESS curve) and significance of the correlation (ns: not significant, (+): p < 0.1, +: p < 0.05, --: p < 0.01, ---: p < 0.001).
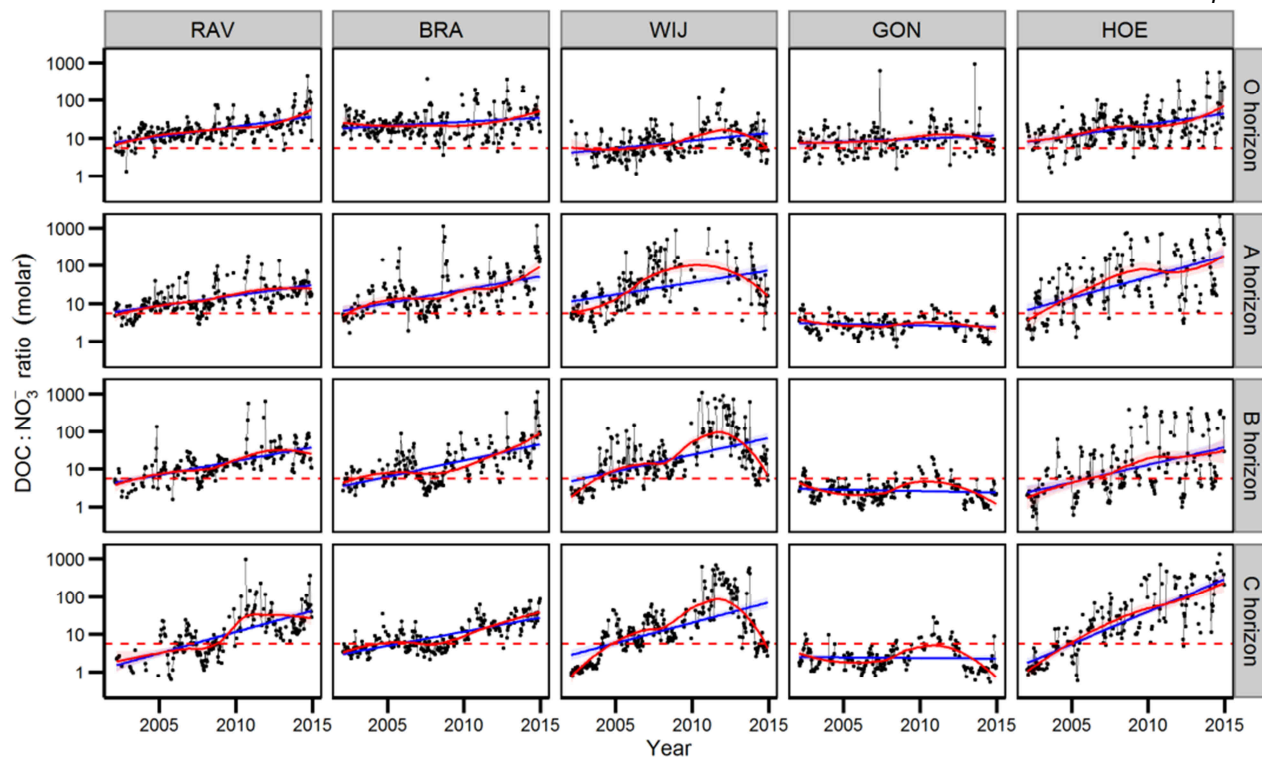
Figure 6.A3 Fortnightly DOC:NO$_3^-$ ratio in soil solution for the five locations, with critical inflection point for soils (DOC:NO$_3^-$ = 5.22) as proposed by Taylor and Townsend (2010) indicated by the red dashed line and trend lines (blue: linear regression line, red: LOESS curve).
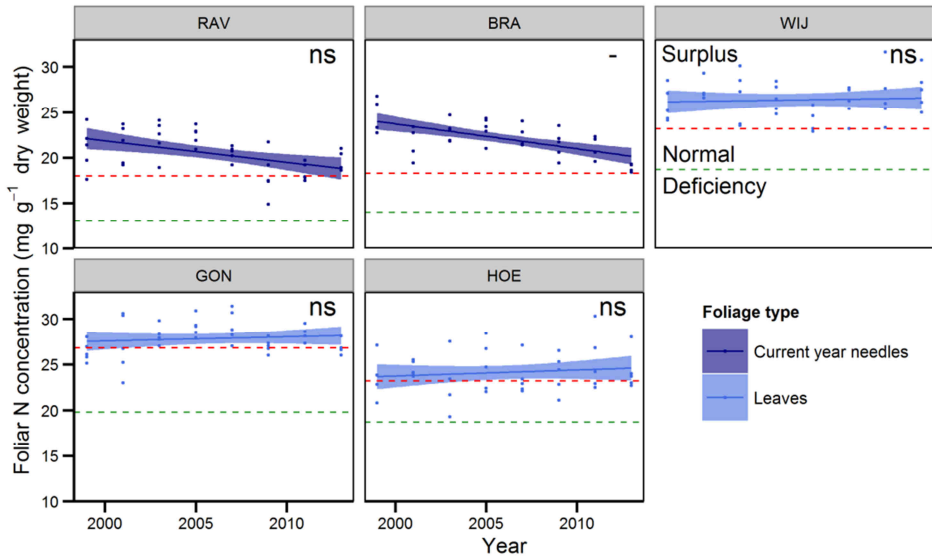
Figure 6.A4 Foliar N concentration for the five locations (1999–2013) with critical lower limit (green) and upper limit (orange) (van den Burg and Schaap, 1995; Mellert and Göttlein, 2012), with significance of Mann-Kendall trends (ns: not significant, -: p < 0.05).
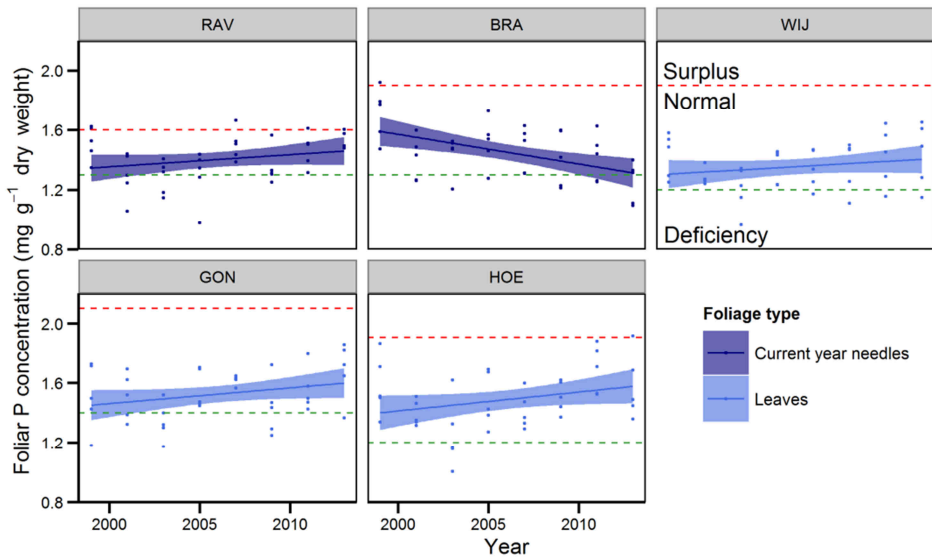
Figure 6.A5 Foliar P concentration for the five locations (1999–2013) with critical lower limit (green) and upper limit (orange) (van den Burg and Schaap, 1995; Mellert and Göttlein, 2012). Trends were not significant.

7   **GENERAL DISCUSSION AND CONCLUSIONS**

7.1   **Is air pollution abatement policy in Flanders on target with respect to forest protection?**

7.1.1   Deposition targets

Throughfall depositions of potentially acidifying and eutrophying compounds (non-marine SO_4^{2-} and NH_4^+) sharply decreased in five ICP Forests Level II plots in Flanders between 1994 and 2010 (see Chapter 3). Plotting these long-term deposition trends against target values for forest ecosystems included in (inter)national legislation allows to evaluate the effectiveness of local emission reduction policy.

Acidifying deposition

In Flanders, a general mid-term target for acidifying depositions was set for 2010 (2660 acid equivalents ha^{-1} yr^{-1}) based on the objectives for emission levels of NO_x, SO_2 and NH_3 agreed at the European level and included in the National Emission Ceilings (NEC)-Directive 2001/81/EG (EU, 2001; Vlaamse overheid, 2003; Buysse et al., 2010). The 2010-target of the NEC-Directive was about reached in time in all Level II plots (Figure 7.1).

Long-term targets (2030) for acidifying depositions and inorganic N depositions were included in VLAREM II, Appendix 2.4.2 (Table 7.1) (Vlaamse overheid, 1995). In the three deciduous forest Level II plots the 2030-target was already reached in 2015 (Figure 7.1). In the two coniferous forest plots 2015 TF and total acidifying depositions were still above the 2030-target, but if the current decreasing trends are continued it is very likely reached in the next few years.

Table 7.1 Long-term targets (2030) for acidifying and inorganic N depositions (equivalents ha^{-1} yr^{-1}) in forests included in VLAREM II, Appendix 2.4.2 (Vlaamse overheid, 1995).

Compounds	Equivalents ha^{-1} yr^{-1}	Forest type
Acidifying	1400	Coniferous forest on sandy soil
Acidifying	1800	Deciduous forest on poor sandy soil
Acidifying	2400	Deciduous forest on rich soil
Inorganic N	1000 (14 kg N)	Deciduous forest
Inorganic N	400 (5.6 kg N)	More natural species composition in coniferous forest

Figure 7.1 Annual TF and total deposition calculated with the Canopy Budget Model of Ulrich (Ulrich, 1983; Draaijers and Erisman, 1995) of acidifying compounds (H$^+$ + non-marine SO$_4^{2-}$ + NH$_4^+$ + NO$_3^-$) in the five Level II plots (1994–2015) compared to the 2010-target value of the NEC-Directive 2001/81/EG for total acidifying deposition on forests (2660 acid equivalents, yellow dashed line) and the 2030-target value of the MINA-plan (VLAREM II) (coniferous forest: 1400 acid equivalents ha^{-1} yr^{-1}, deciduous forest on chemically poor soil: 1800 acid equivalents ha^{-1} yr^{-1}, deciduous forest on chemically rich soil: 2400 acid equivalents ha^{-1} yr^{-1}, red dashed line) (Vlaamse overheid, 2003; Buysse et al., 2010).

N deposition

The 2030-targets for total inorganic N depositions in 2015 were met in the HOE site only
(Figure 7.2). In the other two deciduous forest plots total inorganic N depositions
remained slightly above the 2030-target but will very likely drop below it in the next few
years. In the coniferous forest plots total inorganic N depositions are still about three
times the 2030-target, i.e. far above the level that would allow the re-establishment of a
more natural species composition (Figure 7.2).

Figure 7.2 Annual TF and total deposition calculated with the Canopy Budget Model of
Ulrich (Ulrich, 1983; Draaijers and Erisman, 1995) of inorganic N ($NH_4^+ + NO_3^-$) in the five
Level II plots (1994–2015) compared to the 2030-target value of the MINA-plan (VLAREM
II) (deciduous forest: 1000 equivalents ha^{-1} yr^{-1}, more natural species composition in
coniferous forest: 400 equivalents ha^{-1} yr^{-1}, indicated by the red dashed line) (Vlaamse
overheid, 1995).

7.1.2   Critical loads for inorganic N

The new NEC-Directive 2016/2284/EU includes the requirement to monitor air pollution impacts on forest ecosystems in Flanders, with the long-term objective of not exceeding critical loads and levels (EU, 2016). Even though the five Level II plots do not fully spatially represent Flemish forests, the long-term data collected from these plots is the current best means available.

Despite the substantial decrease in NH_4^+ depositions over the past two decades, in 2015 TF and total deposition of inorganic N in the RAV and the BRA site still exceeded the upper limit of the empirical critical N load range of 5 to 15 kg N ha^{-1} yr^{-1} for coniferous woodland as proposed by Bobbink and Hettelingh (2011) (Figure 7.3). In the three deciduous forest plots, TF and total deposition of inorganic N initially also exceeded the empirical critical load range of 10 to 20 kg N ha^{-1} yr^{-1} for broadleaved deciduous woodland as proposed by Bobbink and Hettelingh (2011), but were within this range during the last decade of the monitoring period (Figure 7.3). It therefore looks like the critical loads targets for ground vegetation will be reached in the next few years.

More stringent critical loads targets have been proposed for specific groups, viz. ectomycorrhizal fungi and epiphytic lichens. The deposition of inorganic N in the GON site was higher than the empirical critical load range of 9.5–13.5 kg N ha^{-1} yr^{-1} for ectomycorrhizal fungi of European oak forests as proposed by Suz et al. (2014), except for TF of inorganic N in 2015 (Figure 7.3). However, recent research in 105 Level II plots across Europe proposed critical loads as low as 5–6 kg N ha^{-1} yr^{-1} for ectomycorrhizal fungi in beech, Scots pine and Norway spruce forests (van der Linde et al., unpublished results). These were also not reached at HOE or WIJ. Epiphytic lichens are even more sensitive to N eutrophication (Conti and Cecchetti, 2001) and TF inorganic N loads were as much as 4.4 to 9.5 times the severe critical N load target of 2.4 kg N ha^{-1} yr^{-1} for European forests (Giordani et al., 2014) (Figure 7.3).

The seemingly general positive evolution in N loads in these forests will thus continuously need to be re-evaluated against new critical loads emerging from new scientific insights. In order to fully protect temperate forest ecosystems from any potential negative effects of eutrophication, total N depositions should reach below the critical loads for the most sensitive species groups. Considering current trends of inorganic N deposition it will be very difficult to reach such targets.
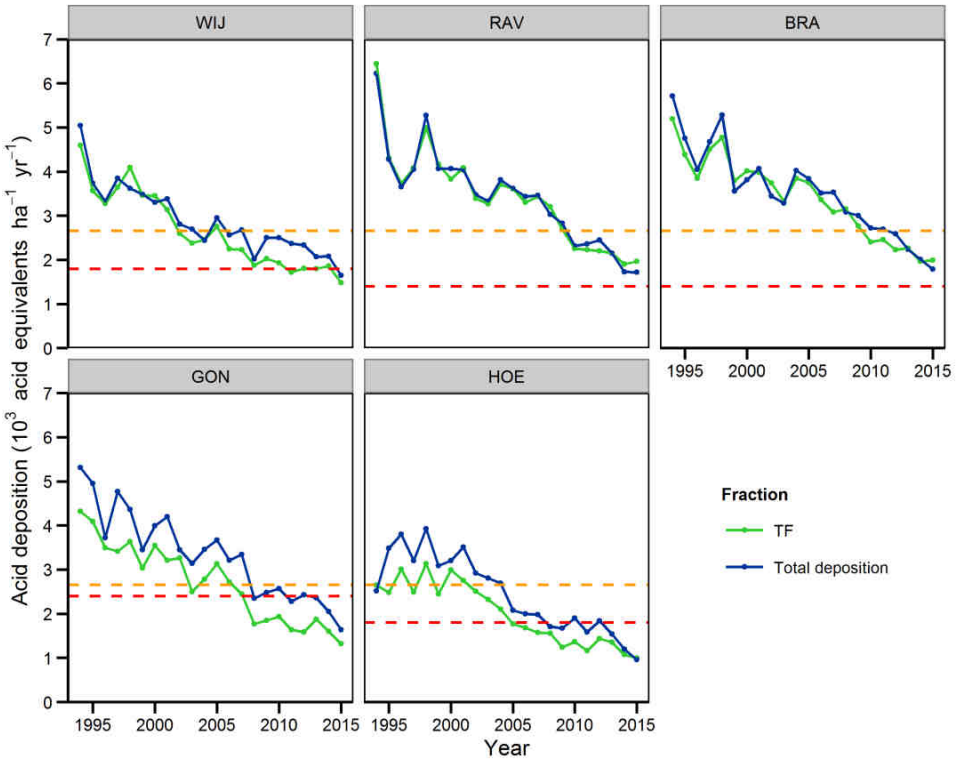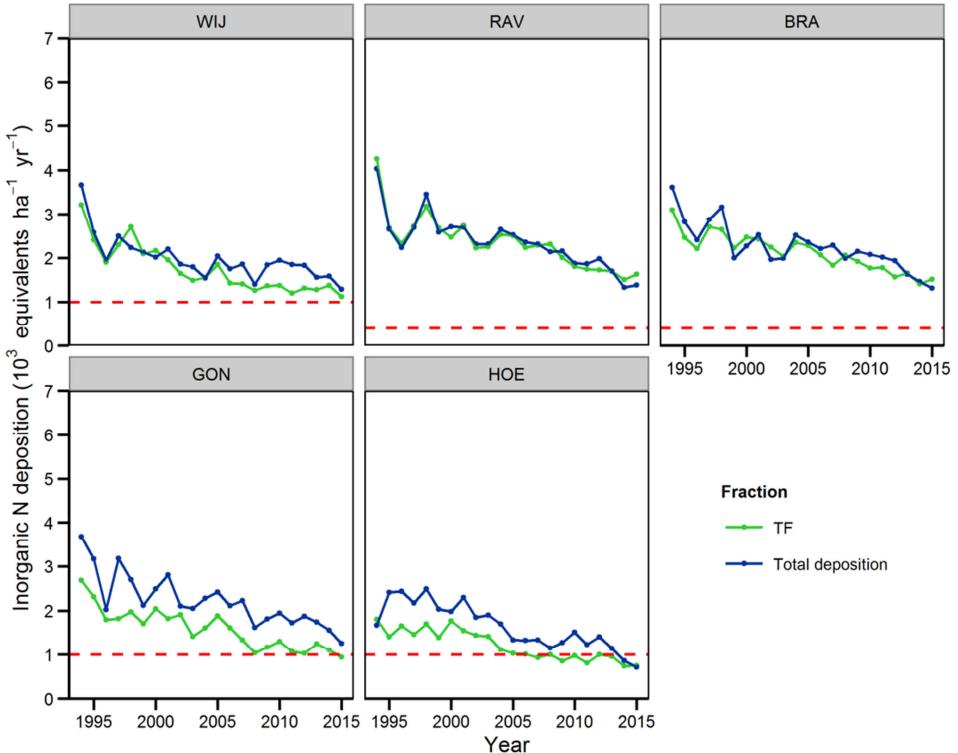
Figure 7.3 Annual TF and total deposition calculated with the Canopy Budget Model of Ulrich (Ulrich, 1983; Draaijers and Erisman, 1995) of inorganic N (NH_4^+ + NO_3^-) in the five Level II plots (1994–2015) compared to the critical load range for ground vegetation in temperate forests (yellow dashed lines) (Bobbink and Hettelingh, 2011) and ectomycorrhizal fungi in European temperate oak forests (red dashed lines) (Suz et al., 2014) and the critical load for epiphytic lichens in European forests (purple dashed line) (Giordani et al., 2014).

7.1.3 Linking depositions and emissions

As explained in Chapter 3, among all deposited ions non-marine SO_4^{2-} showed the sharpest decrease in TF between 1994 and 2010. 1994–2015 trends in annual TF of non-marine SO_4^2 matched well with the decreasing trends of annual SO_2 emissions reported for Flanders and both were correlated (ρ_S = 0.975, p < 0.0001) (Figure 7.4). The TF of NH_4^+ decreased to a slightly lesser extent, and was again synchronous to decreasing trends in annual NH_3 emissions reported for Flanders during this period (ρ_S = 0.914, p < 0.0001) (Figure 7.4). On the other hand, TF of NO_3^- decreased only during the first two years of monitoring (1994–1996) but then stabilized. This contrasts with the gradual

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reported decrease in annual NO_x emissions by as much as 47% in Flanders between 1994 and 2015 and there existed no correlation with annual TF NO_3^- (Figure 7.4) (VMM, 2011, 2016a). Also model calculations (Vlops version 17) based on EMEP emission data from Europe and Belgium suggest a 23% decrease in NO_y deposition in Flanders over the last ten years (VMM, 2017), clearly not reflected by the constant TF NO_3^- loads. A similar inconsistency between national NO_x emissions and the TF of NO_3^- was found in France (Pascaud et al., 2016), suggesting a more general pattern.
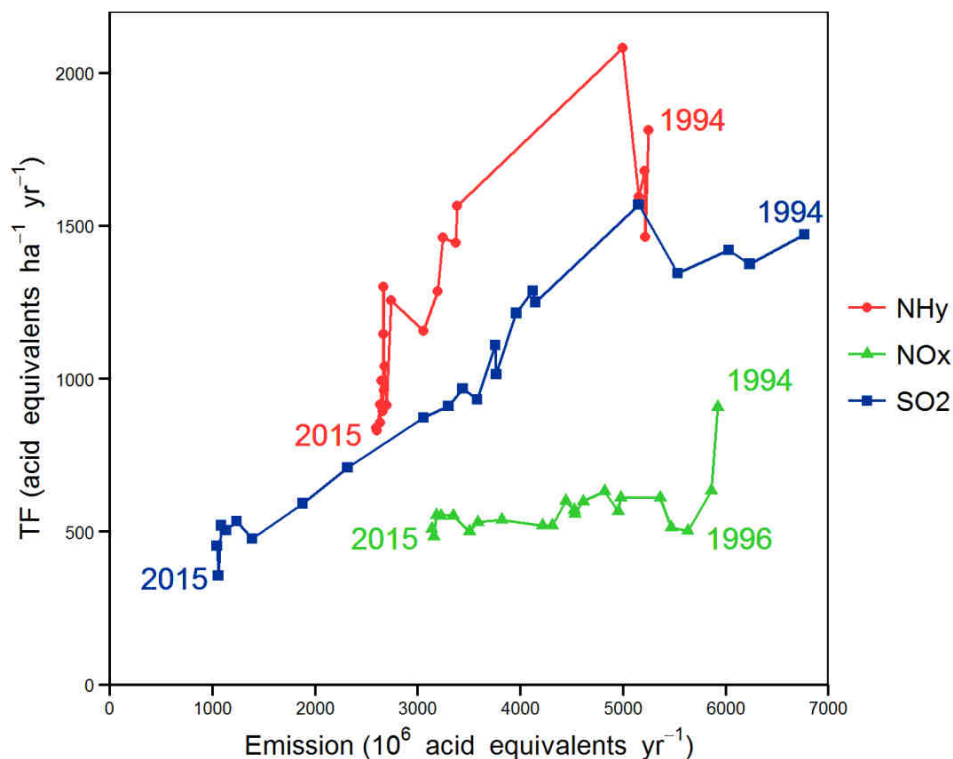
Figure 7.4 Mean annual TF of NH_4^+, NO_3^- and non-marine SO_4^{2-} in the five Level II plots in function of emissions of NH_3, NO_x and SO_2 reported for Flanders (1994–2015) (VMM, 2011, 2016a). The TF of NO_3^- has stabilized since 1996.

The decreasing TF of NH_4^+ and nearly stable TF of NO_3^- resulted in a significant declining trend of the molar NH_4^+:NO_3^- ratio in TF in the five Level II plots (from 2.25 to 1.45, $p < 0.0001$) (Chapter 3, Figure 7.5). Also the BD of NH_4^+ decreased faster than the BD of NO_3^-, likewise resulting in a significant declining trend of the NH_4^+:NO_3^- ratio in precipitation collected in the open field (from 1.87 to 1.4, $p < 0.05$ in RAV and BRA, $p <$

0.01 in GON, p < 0.0001 in WIJ and HOE) (Figure 7.5). These findings agree with the trends observed at monitoring stations located in open habitats in background areas in Flanders operated by the Flemish Environment Agency (www.vmm.be): in six out of nine stations, the slope of the linear time trend (2002–2009) for wet deposition was more negative for NH_4^+ than for NO_3^- (Staelens et al., 2012). However, trends were not yet significant, probably because the time series was still shorter than the minimal nine-year detection period suggested by Waldner et al. (2014).
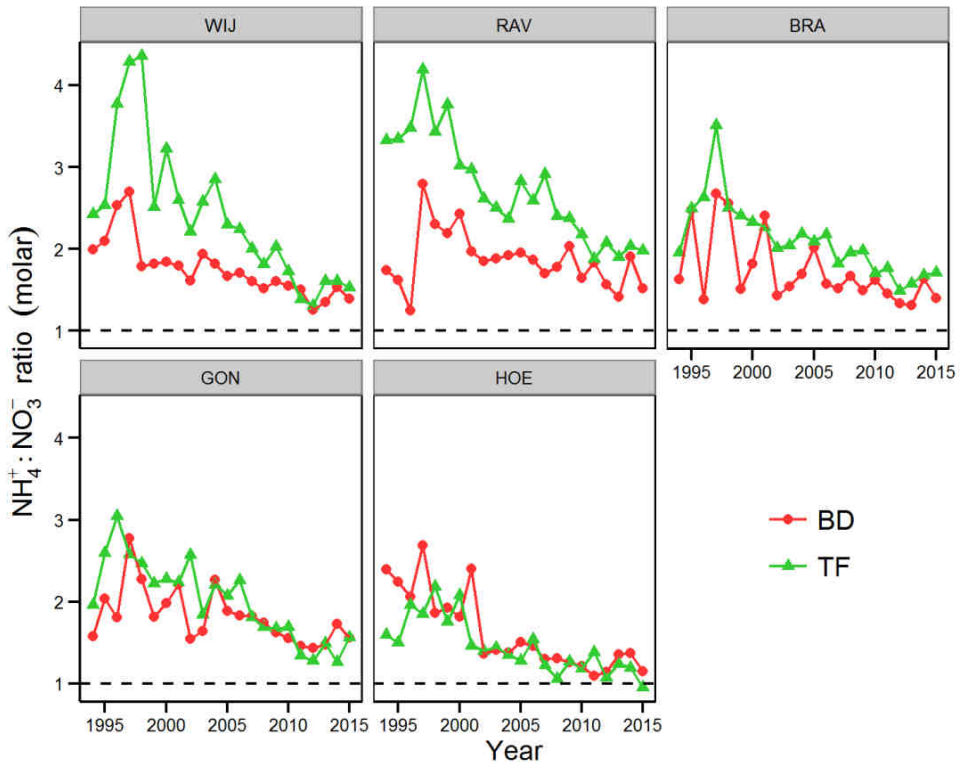
Figure 7.5 Mean annual NH_4^+:NO_3^- ratio (molar) in BD and TF in the five Level II plots in Flanders (1994–2015). The black dashed line marks the 1:1 ratio.

Decreasing trends of the NH_4^+:NO_3^- ratios in precipitation under decreasing inorganic N depositions have been observed particularly in a relatively small part of NW-central Europe, including Flanders and parts of France, northern Italy and northern Germany (Pascaud et al., 2016; Schmitz et al., 2017). In most other European regions the NH_4^+:NO_3^- ratios are instead stable or even increase under decreasing inorganic N depositions. For example, in the Czech republic and Poland NO_x emissions were reduced

faster than NH_3 emissions (Hůnová et al., 2017; Kurzyca and Frankowski, 2017). Also, in Scandinavia and the Mediterranean NH_4^+ depositions are slightly increasing (Schmitz et al., 2017; Vanguelova et al., 2017). At the European scale, Flanders could thus be considered as a specific case with regard to inorganic N depositions. This may be explained by Flanders' extraordinary long pollution history (see Section 1.1.2) as a result of its economically strategic position involving intensive transit road transport, high population density and a concentration of intensive animal husbandry. Consequently, the number of cars is further increasing and vehicle emissions are responsible for the majority of NO_x emissions in Flanders (Table 7.2).

Table 7.2 Contribution (%) of the different sectors to NO_x emissions in Flanders in 2016 (preliminary results) (VMM, 2017).

Sector	Contribution (%)
Households	5
Industry	18
Energy production	5
Traffic	61
Off-road	2
Agriculture and horticulture	7
Trade and services	2

Our results to the least indicate that the relative importance of NH_3 compared to NO_x as an air pollutant generally decreased in Flanders between 1994 and 2015, reflecting the success of measures to reduce NH_3 emissions imposed on the agricultural sector since the 1990s. Particularly this was effectuated by large scale adoption of low-NH_3-emission stables, low-emission application of animal slurry and a slight decrease in livestock numbers, and also the decreasing co-deposition of NH_4^+ with SO_4^{2-} (see Chapters 3 and 6). On the contrary, the TF of NO_3^- stabilized since 1996 at 531 acid equivalents (7.44 kg N) ha^{-1} yr^{-1} on average over the last five years (2011–2015) in the Level II plots (Figure 7.4). This means that NO_3^- deposition alone would probably already exceed critical loads for sensitive ectomycorrhizal fungi and epiphytic lichen species in a number of forests (see section 7.1.2). The latter indicates that current N emission abatement policy in Flanders, which includes emission ceilings for NO_x and NH_3 (Vlaamse overheid, 2003), so far did not yield the expected reduction in depositions of oxidized N compounds, despite the reported drop in NO_x emissions.

The contradiction between the decreasing NO_x emissions and the stable BD and TF of NO_3^- and decreasing NH_4^+:NO_3^- ratio in the Flemish Level II plots may be explained in various ways.

1° Firstly, while TF is calculated from measured concentrations and volumes, national NO_x emissions are but estimates, often based on the emissions from cars tested under laboratory conditions (http://www.emep.int/). As revealed on 18th September 2015 by the "dieselgate" scandal, cars with a diesel engine appeared to emit 6–7 times more NO_x under realistic road conditions (on average for 30 different tested vehicles) (ICCT, 2016). In Belgium, the number of cars with a diesel engine increased rapidly after 1977 and diesel cars have dominated the vehicle park since 2006 (with a peak of 63% in 2013) (Figure 7.6), i.e. laboratory tests may have strongly underestimated traffic-derived NO_x emissions in the past decades, despite the use of correction factors for road conditions (Brouwers et al., 2017).

2° Besides by an underestimation of the emissions from road transport, the inconsistency between NO_x emissions and the BD and TF of NO_3^- could also be partly explained by the complex atmospheric physico-chemical processes that influence the concentrations of oxidized N species in the air (Pascaud et al., 2016). Depending on the atmospheric conditions (incoming radiation, temperature, ...), nitric oxide (NO) and NO_2 can be physico-chemically transformed through reaction with other molecules (e.g. H_2O, O_3, O_2, organics), to form a large array of N compounds, including nitrous oxide (HNO_2 or HONO), nitric acid (HNO_3), dinitrogen pentoxide (N_2O_5) and peroxyacetyl nitrates (PAN) (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). These intermediate compounds can act as temporary sinks in the atmosphere, before the oxidized N is finally removed, principally by wet deposition (dissolved HNO_3 and nitrates). The relationship between emissions and depositions is thus not straightforward. Except NO_x concentrations, which are decreasing (VMM, 2016b), the air concentrations of such intermediate N compounds have not been measured in Flanders. Only since 2016, the Flemish Environment Agency also measures the air concentrations of HNO_3 (VMM, 2017). This lack of data on atmospheric intermediates between NO_x and BD or TF N is a substantial knowledge gap that complicates the interpretation of the link between NO_x emissions and N depositions in Flanders.
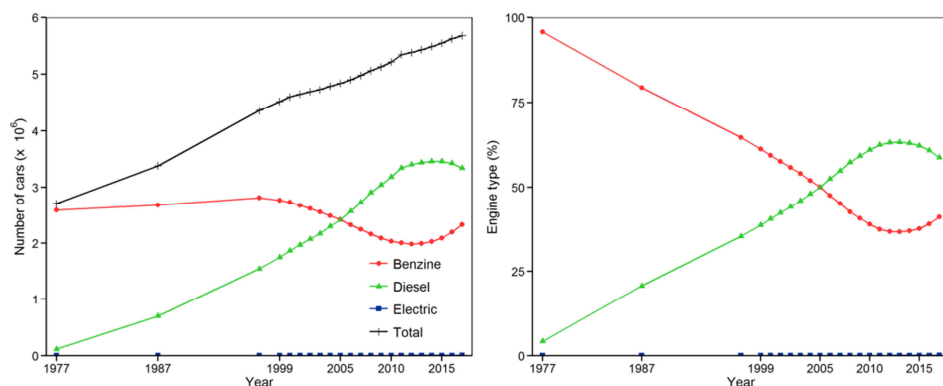
Figure 7.6 Evolution (1977–2017) of the number of cars registered in Belgium per engine type (left) and in percentage (right). Source: http://statbel.fgov.be/nl/statistieken/cijfers/verkeer_vervoer/verkeer/voertuigpark/.

3° A number of underexplored canopy and soil processes could also help to explain the inconsistency between NO_x emissions and BD or TF of NO_3^-. First, re-emission of NH_3 has been observed from the ground during leaf fall and from the forest canopy in the BRA site (Neirynck and Ceulemans, 2008; Hansen et al., 2017). A second process typically occurring in N-saturated forests is soil emission of NO, which could subsequently interact with the canopy (Neirynck et al., 2007). A third and possibly the most important process is bacterial conversion of NH_4^+ to NO_3^- (nitrification) in the canopy (Guerrieri et al., 2015). Using natural abundance oxygen isotope analysis ($\Delta^{17}O$, $\delta^{18}O$), these authors found that a considerable fraction (27–34%, average for the two isotopes) of the TF NO_3^- in a beech stand and a Scots pine stand in the UK originated from canopy nitrification. A more extensive investigation on twelve European Level II plots, including the BRA (Scots pine) and the HOE site (beech) is on-going (Guerrieri et al., unpublished results). However, to keep TF NO_3^- at a stable level under decreasing BD of inorganic N (INBO, unpublished results) and NO_x emissions, the proportion of TF NO_3^- originating from canopy nitrification should have doubled between 1994 and 2015. Regardless of the evolution in canopy uptake of NH_4^+ by the trees, which has not been measured, this is highly unlikely considering that NH_y emissions and the TF and BD (INBO, unpublished results) of NH_4^+ sharply decreased (less NH_4^+ available for canopy nitrification).

4 N compounds can be transported over large distances through the atmosphere. In Flanders, an estimated 50% of the acidifying air pollutants is furthermore imported from neighbouring countries (data 2012) (VMM, 2015) and long-distance transport is

particularly more important for NO_x and SO_2 than for NH_3 (Hov et al., 1994). But emissions and air concentrations of NO_x are also decreasing in the neighbouring countries (van Dril and Elzenga, 2005; Carslaw et al., 2011; Pascaud et al., 2016), which makes an increasing import of NO_x into Flanders unlikely over the study period. Lastly, it has to be kept in mind that the Level II plots are not fully spatially representative (Schmitz et al., 2017) for Flanders as a whole.

Programmatic Approach to Nitrogen (PAS)

In 2014, the Flemish government launched the 'Programmatic Approach to Nitrogen' under the EU Habitats Directive (PAS, https://www.natura2000.vlaanderen.be/pas), aimed mainly at further reducing N emissions to ensure conservation of protected Natura 2000 habitats (12.3% of the area of Flanders) by 2050. The focus of the PAS is at present predominantly on a further reduction of NH_3 emissions by the agricultural sector. It puts restrictions on the extension of activities near and in protected areas, because NH_3 is deposited at a short distance from its emission source. PAS provides subsidies for general measures to reduce NH_3 emissions from existing farms and stables. With respect to NO_x, general measures to reduce background emissions from road transport, the energy and industry sector and households in the PAS are included in the "business as usual" scenario (BAU2030). However, the BAU2030-scenario also includes the assumption that NO_x emissions are currently decreasing and will continue to do so in the near future (https://www.natura2000.vlaanderen.be/pas-beslissing-van-30112016). Bearing in mind the "dieselgate" scandal and the nearly stable trends of the BD and TF of NO_3^- in the Level II plots observed in this study, this BAU2030-scenario likely is too optimistic, suggesting that the measures in the PAS will not be sufficient to protect Natura 2000 forest habitats. The results from this thesis suggest that the PAS may particularly not achieve its target for oxidized N compounds and that additional measures will be necessary to bring NO_x emissions to an acceptable level. Such additional measures should be directed in the first place to reducing the exhaust from traffic.

7.2   **Actual trends and prospects for recovery from acidification and N saturation**

7.2.1   Do we already see a recovery from acidification and eutrophication in Flemish forests?

The main aim of this thesis was to evaluate recent evolutions in the chemical soil (water) quality and tree mineral nutrition in Flemish forests and, more specifically, to check whether the rates of acidification and eutrophication are slowing down or recovery has started in response to decreasing anthropogenic emissions of SO_2, NH_3 and NO_x.

The decreasing external inputs with TF of potentially acidifying and eutrophying compounds (particularly non-marine SO_4^{2-} and NH_4^+) resulted in decreasing trends of the ionic strength and the concentrations of SO_4^{2-}, NO_3^- and Al_{tot} in the soil solution at the five Flemish Level II plots (Chapter 3). Thereby, the molar DON:TDN ratios and DOC:NO_3^- ratios in soil solution showed increasing trends over the period studied, indicating an improving forest abiotic N status (Chapter 6). Simultaneously, the pH of the soil solution in the mineral soil further decreased until 2004, but then reclined and increased by about 0.5 units in the decade thereafter (Chapter 5). On the other hand, soil solution molar BC:Al_{tot} ratios showed decreasing trends in three plots, and soil solution ANC is, despite the overall increasing trend, still negative (Chapter 3). Nevertheless, the slight increase in pH and, more importantly, the strong decrease in ionic strength, seemed to have enhanced OM solubility, evidenced by increasing trends of soil solution DOC and DON concentrations over the past decade (Chapters 4 and 5). The impact was stronger for DON than for DOC, resulting in consequent declining molar DOC:DON ratios, particularly in the O horizon and the upper mineral soil (Chapter 5). Hence, increasing molar DON:TDN ratios and DOC:NO_3^- ratios did partially result from higher OM solubilisation (Chapter 6), and so care needs to be taken when interpreting these trends as indicative of forest N status. In fact, soil solution NO_3^- concentrations were still above the critical limit of 1 mg N L^{-1} for elevated NO_3^- leaching/N saturation (Iost et al., 2012; Waldner et al., 2015) at the critical inflection point for the DOC:NO_3^- ratio (5.22) as proposed by Taylor and Townsend (2010) (Chapter 6). Overall, changes in soil solution chemistry thus indicate an onset of abiotic recovery, i.e. an improvement in forest N status, but soil solution acidification is still continuing albeit at decreasing rates.

Foliar N concentrations in the five Level II plots remained near or above the critical limits determined by Mellert and Göttlein (2012), indicating luxury consumption of N by the trees, while P nutrition generally was in the lower part of the normal range, and tending towards latent deficiency at the BRA site (Chapter 6). The foliar N:P ratio and BC:N ratio also remained unchanged in the Level II plots between 1999 and 2013, pointing to a nearly stable but unbalanced tree nutritional status (Chapter 6). At present, biotic recovery is thus lagging behind on the generally positive changes in soil solution chemistry.

The results of this study broadly agree with the findings of similar trend studies using data from long-term monitoring sites in Europe and the US, which also observed a slowing down of soil solution acidification in response to the overall decrease in SO_2 emissions and SO_4^{2-} depositions (Table 7.3). With regard to the evolution in forest abiotic N status this study found generally stronger changes in soil solution chemistry than similar trend studies, probably because TF DIN depositions decreased at a higher rate (2.4–5.0% yr^{-1}) than the European average of 1.3–1.8% calculated by Waldner et al. (2014) (Chapter 6).

Table 7.3 Overview of the evolution in soil solution and foliar chemistry found in this study in comparison to similar studies using data from long-term monitoring sites in Europe and the US. Symbols: ↑: increasing trend, ↓: decreasing trend, ↔: stable trend or inconsistent trends.

Effect	Trend		
	This study	Similar studies	
Soil solution			
pH	↑	↑	Akselsson et al. (2013), Löfgren et al. (2011) (Sweden)
		↔ / ↑	Vanguelova et al. (2010), Sawicka et al. (2016) (UK), Fölster et al. (2003), Löfgren and Zetterberg (2011), Pihl Karlsson et al. (2011) (Sweden) Johnson et al. (2013) (Ireland)
		↓	Boxman et al. (2008) (Netherlands), Jonard et al. (2012) (Wallonia), Fuss et al. (2011) (US)
SO_4^{2-}	↓	↓	Borken et al. (2011), Meesenburg et al. (2016) (Germany), Jonard et al. (2012) (Wallonia), Boxman et al. (2008) (Netherlands), Vanguelova et al. (2010), Sawicka et al. (2016) (UK), Graf Pannatier et al. (2011) (Switzerland), Akselsson et al. (2013), Fölster et al. (2003), Löfgren et al. (2011), Löfgren and Zetterberg (2011), Pihl Karlsson et al. (2011) (Sweden), Ukonmaanaho et al. (2014) (Finland), Johnson et al. (2013) (Ireland), Fuss et al. (2011) (US)
NO_3^-	↓	↓	Boxman et al. (2008) (Netherlands), Oulehle et al. (2011) (Czech republic), Fuss et al. (2011) (US)
		↔ / ↓	Graf Pannatier et al. (2011) (Switzerland), Ukonmaanaho et al. (2014) (Finland), Sawicka et al. (2016) (UK)
		↔	Vanguelova et al. (2010) (UK), Löfgren and Zetterberg (2011), Pihl Karlsson et al. (2011) (Sweden), Johnson et al. (2013) (Ireland)
		↔ / ↑	Meesenburg et al. (2016) (Germany)
		↑	Jonard et al. (2012) (Wallonia)
BC	↓	↓	Jonard et al. (2012) (Wallonia), Boxman et al. (2008) (Netherlands), Fölster et al. (2003), Akselsson et al. (2013) (Sweden), Fuss et al. (2011) (US)
		↔ / ↓	Graf Pannatier et al. (2011) (Switzerland), Sawicka et al. (2016) (UK)
		↔	Vanguelova et al. (2010) (UK), Johnson et al. (2013) (Ireland)
Al_{tot}	↓	↓	Boxman et al. (2008) (Netherlands), Fuss et al. (2011) (US)
		↔ / ↓	Vanguelova et al. (2010) (UK), Johnson et al. (2013) (Ireland), Löfgren et al. (2011), Löfgren and Zetterberg (2011), Pihl Karlsson et al. (2011) (Sweden)
		↔	Sawicka et al. (2016) (UK)
		↑	Jonard et al. (2012) (Wallonia), Fölster et al. (2003) (Sweden)
$BC:Al_{tot}$	↓		
		↔ / ↓	Graf Pannatier et al. (2011) (Switzerland)
		↔ / ↑	Meesenburg et al. (2016) (Germany)

Table **7.3** continued.

Effect	Trend		
	This study	Similar studies	
ANC	↑ (< 0)	↑ (< 0)	Akselsson et al. (2013), Löfgren et al. (2011) (Sweden), Fuss et al. (2011) (US)
		↔ / ↑	Fölster et al. (2003), Löfgren and Zetterberg (2011), Pihl Karlsson et al. (2011) (Sweden)
Ionic strength	↓	↓	Löfgren et al. (2011) (Sweden), Vanguelova et al. (2010) (UK)
		↔ / ↓	Löfgren and Zetterberg (2011) (Sweden)
DOC	↑	↑	Vanguelova et al. (2010), Sawicka et al. (2016) (UK), Oulehle et al. (2011) (Czech republic), Borken et al. (2011) (O horizon, Germany)
		↔ / ↑	Johnson et al. (2013) (Ireland)
		↔	Ukonmaanaho et al. (2014) (Finland), Borken et al. (2011) (upper mineral soil, Germany)
		↔ / ↓	Löfgren and Zetterberg (2011) (Sweden), Fuss et al. (2011) (US)
		↓	Akselsson et al. (2013), Löfgren et al. (2011) (Sweden), Clarke and Lindroos (2010) (Norway), Borken et al. (2011) (deeper mineral soil, Germany)
DON	↑	↑	Vanguelova et al. (2010) (UK), Oulehle et al. (2011) (Czech republic)
Foliage			
N	↔	↔	Jonard et al. (2012) (Wallonia), Jonard et al. (2015) (Europe)
		↓	Oulehle et al. (2011) (Czech republic), McNulty et al. (2017) (US)
P	↔	↓	Jonard et al. (2012) (Wallonia), Jonard et al. (2015) (Europe)
N:P	↔	↑	Jonard et al. (2012) (Wallonia), Jonard et al. (2015) (Europe)
BC:N	↔	↓	Meesenburg et al. (2016) (Germany)

7.2.2   On what term, if at all, could we expect a substantial recovery?

A burning question from both a scientific point of view and for forest managers and policy makers is how fast, if at all, forests in Flanders could substantially recover from acidification and eutrophication.

Until now long-term trends of SO_4^{2-} and NH_4^+ depositions in the five Level II plots decreased approximately linearly, suggesting that deposition targets will be reached and critical loads for ground vegetation will be respected within the next few years (Chapter 3, section 7.1.2). However, the increasing marginal cost to further reduce emissions could cause deposition trends to increasingly level off, as already observed in the UK (Sawicka et al., 2016). Since 2010, the air concentrations of SO_2 in the BRA site are stagnating (Cools et al., 2016) and the same holds for the air concentrations of NH_3 at 17 Flemish

monitoring stations in open vegetation since 2008 (VMM, 2017). This may indicate that deposition trends will begin to level off in the near future.

Besides the decreasing BC depositions (Chapter 3), at least two other factors are delaying recovery in Flemish forests. First, the increasing trends of soil solution DOC and DON concentrations (Chapters 4 and 5) might have led to an increasing organic acid concentrations, which might partly counterbalance the decrease in acidifying depositions (Johnson et al., 2013). At present, the pH-CaCl$_2$ in most soils is about 3.5–4.5, and so pH-H$_2$O is likely still partly below the pKa of carboxylic groups (4-6). Consequently, a large share of these SOM constituents will release protons into soil solution as pH increases, countering recovery from acidification. This delaying effect would be larger in soil with more OM. Secondly, large amounts of S and N have accumulated in these forest soils, which have thick forest floors and mineral layers developed in sand and loess deposits, with a relatively high nutrient storage capacity. Accumulation of S was confirmed by the leaching of SO$_4^{2-}$ that exceeded SO$_4^{2-}$ deposition in two Level II plots between 1994 and 2010 (Chapter 3). Hence SO$_4^{2-}$ desorption of previously deposited S, which releases co-adsorbed H$^+$ and comes alongside with higher leaching of neutralizing base cations (Johnson and Reuss, 1984; Gustafsson et al., 2015), is probably also delaying recovery from acidification, as already observed for several other long-term monitoring sites in Europe and the US (Alewell et al., 2000; Oulehle et al., 2006; Akselsson et al., 2013; Fakhraei et al., 2014; Meesenburg et al., 2016). Sulphur can be stored in and released from different pools in forest soils, including organic matter and SO$_4^{2-}$ adsorbed on Al and Fe hydrous oxides (Johnson and Reuss, 1984). Except the total S pool down to a depth of 1 m (Fleck et al., 2016), the size of individual S pools in the Flemish Level II plots has to date not been determined, so predictions of how long and to what extent accumulated S will continue to influence ecosystem processes remain very tentative. The importance of this N and S accumulation in these soils can be seen from comparisons to other soils. E.g. McNulty et al. (2017) demonstrated that after the cessation of a 30-year N addition experiment in a Red spruce stand on soils with very thin A, B, and C horizons, and thus low nutrient storage capacity, recovery of foliar and forest floor N concentrations could be surprisingly fast.

Studies based on long-term forest monitoring data showed that acidifying depositions in the past century caused a strong decline of soil exchangeable BC and that it will probably take decades to restore the buffer capacity (Alewell et al., 2000; Reinds et al., 2009; Meesenburg et al., 2016). It is uncertain whether the depleted soil BC stocks in the

Flemish forests could be naturally restored. Input of BC is from atmospheric deposition (which is decreasing), mineral weathering (which is probably low on these relatively poor and very acidic sand, sandy loam and loam soils), and decomposition of organic matter. Future prospects are probably best for the GON site, where the soil contains more clay in the deeper mineral layers and has maintained a higher base saturation. The same may be true for the BRA site where locally shallow clay lenses are present (Chapter 2).

An often used method to remediate soil degradation caused by acidification and eutrophication is liming with Ca and Mg (Kreutzer, 1995; Geary and Driscoll, 1996; Boxman and Roelofs, 2006; Battles et al., 2014). After dissolution of the liming material the BC are partly retained in the soil, often resulting in a temporary increase in soil pH and ANC (Kreutzer, 1995; Simmons et al., 1996; Meiwes et al., 2002; Nohrstedt, 2002). In Germany, where about half of the forest area has been limed, initial recovery from acidification during the past two decades was more pronounced in forest soils that underwent liming (König et al., 2017). In the Hubbard Brook Experimental Forest, New Hampshire, US tree growth recovered after Ca addition (Battles et al., 2014). The concept of liming in forests is, however, subject of debate, because a number of undesired side effects have been observed. In general, liming also (temporarily) stimulates respiration, mineralisation and nitrification in the upper humus layer, often leading to soil losses of SOM and C and increased NO_3^- leaching, especially in N saturated forests (Belkacem and Nys, 1995; Kreutzer, 1995; Geary and Driscoll, 1996; Simmons et al., 1996; Corre et al., 2003). Higher soil solution NO_3^- concentrations come alongside with increased N availability, which commonly leads to shifts in ground vegetation composition by promoting nitrophilous competitive and ruderal species, particularly when sufficient light penetrates the canopy (Becker et al., 1992; Dulière et al., 1999; De Keersmaeker et al., 2000; Dulière et al., 2000). It is therefore questionable whether liming would be a good measure to mitigate the long-term impacts of acidification and N saturation in Flemish forests. However, to enable recovery the excess of N first has to be removed from the forest ecosystem in some way. Liming may be the only possible method to do this within a reasonable period of time (through increased NO_3^- leaching), however then one should temporarily accept the negative effects mentioned above.

Recovery from acidification did not result immediately in a strong increase in pH, but it generally induced a higher topsoil mobilization of DOC and even more for DON (decreasing DOC:DON ratios), which could be explained mainly by the decreasing soil solution ionic strength, which was linked to decreasing SO_4^{2-} deposition (Chapter 5). This

mobilization of DOC and DON may in time impact DOC inputs into the aquatic cycle (Freeman et al., 2001; 2004; Cole et al., 2007; Battin et al., 2009; Ciais et al., 2013; Lapierre et al., 2013; Regnier et al., 2013), but it should be remarked that this concerns relatively small fluxes (19–61 kg ha^{-1} yr^{-1}). In part transport of DOC to groundwater will also be limited by likely re-adsorption in deeper mineral layers.

For the five Level II plots studied, it is impossible to predict future timing for normalization of foliar N:P ratios because of two main reasons (Chapter 6). Firstly, the on-going soil pH increases are still in the low end of the Al buffer range (pH 4.0 for gibbsite). A relatively small increase in pH, in combination with lowering of ionic strength, could then both abruptly lower soil solution levels of Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ and reduce the formation of organo-metal complexes and increase OM solubility (Monteith et al., 2007; Scheel et al., 2007). This could have positive effects on P availability as well (Kochian et al., 2004). Secondly, the pH of the soil solution and pH-$CaCl_2$ of the mineral soil is currently very low (3.5-4.5) in all studied soils. Since these conditions are in theory unfavourable for soil microorganisms, bacterial activity must be minimal and the observed onset of recovery likely is predominantly chemical (abiotic), as discussed in Chapter 6. However, (heterotrophic) bacterial activity could also increase non-linearly when pH-inflection points are reached and C limitation is being alleviated, which could be reflected by increasing DOC:NO_3^- ratios (Taylor and Townsend, 2010; Helton et al., 2015). If so, NO_3^- levels may increase again due to microbial decomposition of native soil organic matter (Aber et al., 1989), while DOC and DON levels would change in unpredictable directions alongside. Also the diversity of (ecto)mycorrhizal fungi could benefit from a further increase in pH and decreasing N availability (Lilleskov et al., 2002; van Diepen et al., 2007; Cox et al., 2010; Pardo et al., 2011; Kjøller et al., 2012; Suz et al., 2014; De Witte et al., 2017). Regarding the important role of ECM fungi in nutrient uptake (especially P) by the trees this could then also have beneficial effects on tree mineral nutrition (Talkner et al., 2015; De Witte et al., 2017). But as discussed in Chapter 6, changes in the foliar N content should probably not yet be expected in the early stages of recovery from N saturation, given the non-linear response of foliar N concentration in function of N availability (Galloway et al., 2003).

While the legacy from acidification and N saturation may continue to produce after-effects in Flemish forests for decades, the impacts of climate change will be superimposed on this. Using the Standardised Precipitation-Evapotranspiration Index (SPEI), Sousa-Silva et al. (2017) found evidence for a structural desiccation in Flemish forests since 2007,

which increased defoliation in oak and beech plots of the ICP Forests Level I network. More frequent and intense drought and heat waves are suspected to be important drivers of (sudden) tree mortality (Solly et al., 2017) and to strengthen the impact of forest fires (Abatzoglou and Park Williams, 2016; Knorr et al., 2016) and indigenous and invasive pests and diseases (e.g. ash decline, oak decline) (Fischer and Schär, 2010; Brown et al., 2015; 2018). The introduction of invasive species, facilitated by transport and trade, is seen as one of the biggest global challenges and threats for forest health in the coming decades (Brockerhoff, 2017). One general measure that could help to mitigate impacts is to promote mixed forest stands, which were found to be more resilient to the effects of climate change than monocultures (Sousa-Silva et al., 2017).

As explained in a review by Stevens (2016), the response time to changes in inorganic N depositions can vary greatly among ecosystem compartments. Soil solution NO_3^- and NH_4^+ concentrations can normalize relatively rapidly, but vegetation species composition, tree mineral nutrition, below-ground communities and soil processes could take much longer to recover. The results from this study confirm this and suggest that a substantial recovery could take decades, while natural soil buffer capacity will probably not be able to recover without active intervention (e.g., liming).

7.3   **Implications for policy and management**

7.3.1   Air pollution policy

As discussed in sections 7.1 and 7.2 the negative effects of past air pollution on soil solution chemistry and on the mineral nutrition of trees in Flemish forests will likely persist for many decades. Moreover, it was found that air pollution levels are still too high, resulting in inorganic N depositions that are still several times higher than the critical N loads for epiphytic lichens and ectomycorrhizal fungi. While the PAS of the Flemish government is convincing as a strategy to further reduce NH_3 emissions, the results of this thesis indicate that NO_x emissions are currently underestimated and that policy makers should introduce stricter measures to reduce NO_x emissions from traffic to protect Natura 2000 forest habitats by 2050.

7.3.2   Forest management

Apart from laws and regulations, forest managers could take specific actions to minimize excess anthropogenic acidification. Besides the partly controversial option of liming (see

section 0), an adequate selection of the tree species could provide a more natural buffer against soil acidification (Augusto et al., 1998), which may promote the biodiversity of acid-sensitive organisms (e.g. earthworms, plants) (Verstraeten, 2013; Thomaes, 2014; De Wandeler et al., 2016). Tree species with fast degrading litter (low C:N ratio) containing high concentrations of base cations are *Tilia*, *Fraxinus*, *Betula*, *Prunus*, *Carpinus* and *Populus*, while litter from *Quercus*, *Fagus* and coniferous tree species has less favourable properties (Muys and Lust, 1992; Augusto et al., 2002; Verstraeten et al., 2004; De Schrijver et al., 2012). Particularly coniferous trees are less suitable from this point of view because their ever-green character makes them capture more acidifying deposition than deciduous trees (De Schrijver et al., 2004). Caution is needed with N fixing tree species, e.g. *Alnus* species, because this may induce further soil eutrophication and acidification (Dossche, 1998; De Schrijver et al., 2012). But of course litter quality should not be the single criterion to select tree species. Also abiotic site characteristics (soil type, hydrology) and their possible changes in the long term driven by climate change should be taken into account (Albert et al., 2017).

7.3.3   Research policy

This work also illustrates the major added value of long-term monitoring networks like the pan-European ICP Forests Level II network and the global LTER network. The relatively long time series allow for correlative analysis between multiple variables that change alongside (parallel trends), enabling to identify or at least suggest cause-effect relationships and to reveal the long-term effects of changing environmental conditions on forests, which is often not possible within the limited time span of a project-based study. Thanks to the harmonized and highly standardized methods for the collection and analysis of samples the Level II data also offer the possibility to compare results among countries and thus to verify results from local or regional studies at a larger spatial scale. Moreover, the Level II plots also function as active research platforms for additional more detailed and experimental studies, whereby the time series provide valuable background information on the environmental conditions and their changes over time. From a scientific point of view it is therefore paramount that these monitoring networks are maintained in the future, and receive continuing political and financial support from national and international governments.

7.4   **Suggestions for further research**

Over the course of this study it became clear that predictions about recovery from acidification and N saturation in Flemish forests are complicated by several knowledge gaps.

More information is needed about the amount of NH_y captured by the forest canopy via dry deposition, which is likely underestimated by the Canopy Budget Model. Therefore it would be useful to measure the dry deposition of NH_3 at the Level II plots. This could be done indirectly using wet-only collectors in the open field. In combination with the bulk deposition data, the wet deposition data allow to estimate the local dry deposition factor of NH_3 in the open field (Staelens et al., 2005; Balestrini et al., 2007). Currently, one wet-only collector is already operational at the BRA site since 2006.

In order to get a better insight in the complex link between NO_x emissions, NO_y air concentrations and NO_3^- depositions in Flemish forests it would be useful to monitor NO, NO_2 and the intermediate N species that could form a temporary sink in the atmosphere (N_2O_5, HNO_3, HNO_2, PAN and particulate NO_3^-) and O_3 in the open field near the Level II plots. This is possible with passive samplers, as currently done for NH_3 since 2009 and for O_3 (2009–2011) in the Level II plots.

It is also not known how the on-going changes in soil solution chemistry are influencing P availability for the trees in the Level II plots. As mentioned in Chapter 6 on-going possible abrupt lowering of soil solution levels of Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ as soil pH moves out of the Al buffer range could have positive effects on P availability. Given the relatively low foliar P concentrations, which were occasionally even within the P deficiency range in some sites, information about P availability is crucial to evaluate changes in tree nutritional status. It would therefore be useful to measure the different (organic and inorganic) soil P pools based on the analyses performed on the soil samples collected in the plots in 1991, 2004 and 2014. The same accounts for the size of individual soil S pools, which could provide a better insight in how the slow re-release of long term SO_4^{2-} accumulation could negatively influence ecosystem processes. There is thus ample scope for further research on both the soil samples and the data from the Level II sites.

In order to better understand the relative role of recovery from acidification and climate change in changing DOM dynamics, more detailed studies into the driving factors of DOM dynamics in these changing forest ecosystems would be needed. While this study was

not aimed at a detailed mechanistic understanding of formation, degradation and mobilization processes of DOC and DON, we made a first attempt to elucidate this using linear regression models, linear mixed-effects models and structural equation models. Models were evaluated to determine the percentage of variance in DOC and DON concentrations and fluxes that could be explained by different variables decided to be relevant based on literature, including precipitation, soil humidity, soil temperature, SO_4^{2-} and DIN deposition and soil solution pH and ionic strength. However, despite pre-selection of variables to avoid a combination of highly inter-correlated variables in the models, the results were unreliable, because models were fraught with hidden multicollinearity among variables, which could not be resolved due to the very limited number of plots, and therefore this analysis was not elaborated in this PhD-thesis. First steps could be to experimentally establish the relation between pH and ionic strength and i) soil solution Al; ii) nutrient availability (P, K, Ca, Mg, ...); iii) DOC and DON. This will allow us to better evaluate if forwarded hypotheses on causality between lowered ionic strength and increased DOC and DON mobility could be correct. Secondly, it would be relevant to test the response of soil microbial activity to increasing soil pH and lowering ionic strength in acidified Flemish sandy forest soils. Of particular interest could be to test short to medium term response of soil biological activity, N and P availability to liming.

For the present study, soil water fluxes have been calculated from TF and soil solution concentrations using Na^+ as a tracer ion, assuming that uptake by vegetation, adsorption and mineral weathering of Na^+ are negligible. Water fluxes for the BRA site were also calculated by dr. Johan Neirynck using the MetHyd model and this gave comparable results (INBO, unpublished results). The simple Na^+ tracer method thus seems to yield realistic soil water fluxes for these specific plots. Still, it would be useful to further elaborate this topic and to also calculate water fluxes in the future using mechanistic water balance models, as was done e.g. for Flemish forest plots by Sleutel et al. (2009). Use, calibration and validation of such models will be possible with the Frequency Domain Reflectometry (FDR) soil moisture probes that are currently being calibrated in these plots using monthly measurements of the gravimetric soil moisture content during a 2-year period (April 2015 till June 2017).

There are several well documented historical forest liming experiments in Flanders (e.g. in Sonian, Ravels, Pijnven, …) where different liming treatments (various materials and doses) have been applied several decades ago. Revisiting these sites could provide

useful information about the long-term effects of liming on soils and the potentials of liming for an active restoration of Flemish forest soils.

This study clearly showed that soil solution chemical composition responded faster to changes in SO_4^{2-} and inorganic N depositions than foliar nutrient concentrations. It would be interesting to evaluate the evolution of the soil solution $DOC:NO_3^-$ ratio and DON:TDN ratio also at the European scale and to check whether there are signs of recovery also in areas with lower depositions. Regarding the still high soil solution NO_3^- concentrations around the critical level of 5.22 for the soil solution $DOC:NO_3^-$ ratio as proposed by Taylor and Townsend (2010), it would be useful to investigate whether this critical limit needs to be adjusted for European forest soils.

7.5 **Strengths, weaknesses and uncertainties of the methods used**

All research presented in this thesis is based on long-term monitoring data collected in five ICP Forests Level II plots (see section 2.1). While such a small number of plots cannot possibly be fully representative for the entire region of Flanders, the sites were thoroughly pre-screened for being important combinations of soil type and tree species. In that sense, these sites collectively are representative for the major forest types in Flanders. Still, this limited number of plots and the lack of replicates admittedly is a weak point of this study, because local factors which play an important role may be confounded with the factors tree species or soil type when comparing to the other plots or with literature. While bearing these limitations in mind, we are convinced that the results obtained in these plots do allow to make (cautious) generalisations/extrapolations to Flanders' forests at large, and thus make an invaluable contribution to our knowledge of acidification and eutrophication in these ecosystems. Moreover, the representativeness could further be improved by making links to other monitoring networks (e.g. the Level I network, national forest inventories).

The strength of this work is clearly the relatively long time series and consequent fortnightly acquisition of both the deposition and soil solution data, and the judicious statistical analysis and interpretation of the temporal trends. This greatly enhances our understanding of the processes playing when the soils recover from acidification and eutrophication for some specific cases (soil/stand type combinations), although additional research is needed to confirm the importance of internal processes, including mineralization, nitrification, the sources of DOC and DON, etc.

Another point that needs to be addressed is that the Level II network is not static, but has developed and will continue to develop over time. For example, initially only two lysimeters per depth were available, and the pooled sample volume was therefore often too small to enable chemical analysis, resulting in a higher proportion of missing values compared to more recent years (part of the data was excluded from the analysis because of this reason, see section 3.2.4). There were also two changes in the laboratories that conducted the analyses (1988–1998: Laboratory of Soil Science, Ghent University; 1999–2007: Laboratory for Applied Analytic and Physical Chemistry, Ghent University; 2008–present: INBO) and analytical methods and equipment became more sophisticated and accurate over time. Also quality assurance and control within and among laboratories was further fine-tuned and harmonized and checked via periodic ring tests, resulting in an improving performance of the labs, including at INBO. Consequently, data quality gradually improved over time, which may also have influenced the time series and trends.

The modified Kjeldahl method may underestimate the TKN content of samples due to loss of N during sample preparation or incomplete digestion of organic matter in the samples. Because DON was calculated as TKN – NH_4^+ and TDN was calculated as TKN + NO_3^- + NO_2^-, this could also result in an underestimation of DON and TDN. The INBO laboratory, however, always performed very well for TKN in the ring tests, suggesting that this effect was negligible.

The analysis of the data involved a large number of statistical tests, which come along with uncertainties. One main type of error is to detect an effect that is not there (false positives or Type I error) (Sheshkin, 2004). The chance that this error occurs at a significance level (α) of $\alpha = 0.05$ ($p < 0.05$) is 5% (1 in 20). Many of the trends that were found in this thesis were very significant ($p < 0.001$), which means that the number of Type I errors probably is limited.

In this work the assumption was made that measured total aluminium (Al_{tot}) in soil solution occurred entirely as Al^{3+}. While this assumption might be true based on the theory (pH buffer) regarding the very low pH (3.5–4.5) of the soil solution in the mineral soil (Reuss and Johnson, 1986; Ulrich, 1991; Tipping et al., 2002), this was not verified by modelling speciation of Al by including complexation reactions or by measuring Al species. The high concentrations of DOC in the upper soils suggest that a substantial part of Al might be complexed to organic anions. The knowledge of dominant Al species

in soil solution is pertinent to assess the risk of toxicity to plants (Løkke et al., 1996; Brunner and Sperisen, 2013).

In sections 7.1.1 and 7.1.2 total deposition was included to give an idea of the amount of N taken up by the canopy, which is not included in TF deposition. Total deposition was calculated with the Canopy Budget Model of Ulrich (Ulrich, 1983; Draaijers and Erisman, 1995). However, it has to be mentioned that this model involves many assumptions and that the outcome may vary considerably depending on the time step, type of precipitation data and tracer ion used in the model (Adriaenssens et al., 2013).

7.6   **Conclusions**

Analysis of long-term data collected in five Level II plots in Flanders since 1994 showed that air pollution abatement policy resulted in significant decreases of the atmospheric depositions of non-marine SO_4^{2-} and NH_4^+ in Flemish forests, but had little effect on the depositions of NO_3^- during the past two decades. More stringent measures will be needed to reduce NO_x emissions from road transport beyond the targets of the BAU2030-scenario included in the PAS.

Despite the decreasing acidifying and eutrophying depositions, the critical N loads for ground vegetation and certainly for sensitive ectomycorrhizal fungi and epiphytic lichens were still exceeded. Signs of an onset of recovery from acidification and N saturation were observed in the soil solution, including decreasing concentrations of the main pollutants and their counter ions (SO_4^{2-}, NO_3^-, Ca^{2+}, K^+, Mg^{2+}, Al_{tot}) and ionic strength, while DOC, DON, DOC:NO_3^- ratios, DON:TDN ratios and pH increased. Nevertheless, soil solution BC:Al_{tot} ratios were stable or decreasing and the ANC was increasing but overall kept a negative value. Soil solution acidification is thus continuing, be it at decreasing speed, because BC depositions are declining simultaneously and short-term soil buffering processes (SO_4^{2-} desorption, and perhaps increasing organic acid concentrations) are delaying recovery. The critical levels for elevated NO_3^- leaching were also still exceeded at most sites despite that the critical level for the DOC:NO_3^- ratio was no longer surpassed in four plots, indicating that this critical level might need to be adjusted for European forests. The simultaneousness of increasing trends in DOC mobility and changes in N leaching complicates the use of DOC-based indicators to evaluate forest N status. The pH of the soil solution and the pH-$CaCl_2$ of the soil is also still very low (3.5–4.5) and unfavourable for soil microorganisms, suggesting that the

current recovery is purely chemical (abiotic). Moreover, foliar N and P concentrations revealed luxury consumption of N by the trees and relatively low P nutrition (and even temporal P deficiency in a few situations) while N:P ratios were near or above the critical limits, indicating a stable but unbalanced tree mineral nutrition. Biotic recovery is thus lagging behind on the changes in soil solution chemistry.

This study demonstrated, for the first time, that processes of acidification and N saturation in Flemish forests are slowing down, but the road to recovery will be long because of the N depositions that are still relatively high, the legacy effects induced by S and N accumulation in soils, the decreasing input of BC, and the expected increasing impacts of climate change.

SUMMARY

Background

Elevated atmospheric depositions of non-marine SO_4^{2-} and inorganic N, as a consequence of air pollution, resulted in a progressive acidification and N eutrophication of European forest ecosystems since the start of industrialization. In Flanders, one of the high-deposition regions in Europe, forest soils progressively acidified during the second half of the 20th century and exhibited episodic NO_3^- leaching, a typical sign of N saturation. Since the 1980s, international emission abatement protocols were implemented for SO_2 (1985 Helsinki protocol, 1994 Oslo protocol) and later also for inorganic N (1998 Sofia protocol, 1999 Gothenburg multi-pollutant protocol). This resulted in an overall sharp decrease in non-marine SO_4^{2-} depositions in European forests, while inorganic N depositions decreased less rapidly and only in high-deposition areas in central NW-Europe. In areas where acidifying depositions strongly decreased, an onset of recovery from acidification was observed recently in several long-term forest monitoring sites, while the results for ecosystem N status were inconsistent, varying between a tendency towards recovery and increasing N saturation. It is not clear to what degree European forests can ultimately recover from acidification and N eutrophication and how long this will take.

Objectives

This thesis aimed to firstly evaluate the evolution of atmospheric depositions of non-marine SO_4^{2-} and inorganic N in forests in Flanders during the past decades. Secondly we wanted to assess the impact of the evolution in depositions on soil solution chemistry in Flemish forests. Ultimately the aim was to check whether the rates of acidification and N saturation are slowing down or recovery has started.

This thesis bundles a number of results from the intensive forest monitoring network (Level II) in Flanders. The Level II network was established officially in 1994 by the International Co-Operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests, www.icp-forests.net). The long-term data on atmospheric depositions, soil solution chemistry and tree mineral nutrition from five core plots formed the basis of all research presented in this thesis.

Long-term deposition trends

Trend analysis indicated an overall strong decrease in the TF of non-marine SO_4^{2-} (56–68%) and NH_4^+ (40–59%) in all five Level II plots between 1994 and 2010. The TF of NO_3^- decreased between 1994 and 1996, but was stable thereafter. Also the TF of ACID decreased (45–74%), but it was partly offset by a simultaneous decrease in the TF of BC (19–41%). Despite the substantial decrease in acidifying and eutrophying depositions, inorganic N depositions in the Level II plots in 2015 still exceeded critical load ranges for safeguarding ground vegetation and ectomycorrhizal fungi and are still several times higher than the critical load for sensitive epiphytic lichen species.

The decrease in non-marine SO_4^{2-} could be explained by SO_2 emission reduction measures in industry, including the introduction of desulfurized fuels. For NH_4^+ probably the agricultural sector contributed most by reducing NH_3 emissions from stables, transport of manure and its application in the field (introduction of soil injection techniques). But the decreasing NH_4^+ depositions may also be partly the result of a diminished co-deposition with SO_4^{2-}. The stagnation of NO_3^- depositions since 1996 could likely be explained by an underestimation of the NO_x emissions from road transport, since vehicles with a diesel engine (61% of the car fleet in 2015) emit 6–7 more NO_x under road conditions than during standard laboratory testing (the "dieselgate" scandal). There is however a lack of data on the air concentrations of intermediate oxidized N compounds (N_2O_5, HNO_3, HNO_2, PAN and particulate NO_3^-), which makes it difficult to link between NO_x emissions and NO_3^- depositions.

The current Programmatic Approach to Nitrogen (PAS) under the EU Habitats Directive (https://www.natura2000.vlaanderen.be/pas) of the Flemish Government was launched with the intention to further reduce N emissions but is predominantly focused on a further reduction of NH_3 emissions by the agricultural sector. Because of the nearly stable trends of the BD and TF of NO_3^- in the Level II plots, the PAS's BAU2030-scenario is likely too optimistic, and measures included in the PAS will not be sufficient to protect Natura 2000 forest habitats by 2050.

Long-term trends in soil solution

The between 1994 and 2010 decreasing acidifying and eutrophying depositions were paralleled by decreasing ion concentrations in soil solution (NO_3^-, Al_{tot}, SO_4^{2-} and BC) and decreasing ionic strength in the five Level II plots. The pH of the soil solution in the mineral soil further decreased until 2004, but then reclined and increased by about 0.5

units in the decade thereafter. Increasing soil solution pH and decreasing Al concentrations and ionic strength both could explain increasing trends of soil solution DOC concentrations in the O horizon and in the mineral soil between 2002 and 2012. Fluxes of DOC also increased in the O horizon, but were nearly stable in the mineral soil. Soil solution concentrations and fluxes of DON showed similar increasing trends between 2005 and 2013. Apparently DON was more mobile than DOC, probably due to its selective re-adsorption in mineral horizons. The soil solution molar DON:TDN ratio (2005–2014) and the molar DOC:NO_3^- ratio (2002–2014) showed increasing trends. This rise of both ratios was partly the result of DOC and DON mobilization and so not entirely indicative for an improvement in forest soil N status.

The ANC of the soil solution increased but remained negative, indicating that soil solution acidification is slowing down but still continued. Moreover, the soil solution BC:Al$_{tot}$ ratio further decreased in the mineral soil of four plots, probably because the amount of BC leached from the soil is not compensated by the input from decomposition, mineral weathering and decreasing BC depositions. In the three plots on sandy soils with low cation exchange capacity and base saturation, the BC:Al$_{tot}$ ratio still exceeds the critical limit for damage to fine roots, reduced tree stability, inhibited root growth and growth reductions of up to 80% of mean growth. Recovery from acidification was delayed by SO_4^{2-} desorption and perhaps also by increasing organic acid concentrations, as indicated by the increasing soil solution DOC concentrations.

The observed changes in the soil solution likely are purely chemical (abiotic), regarding the still very low soil solution pH and pH-$CaCl_2$ in the mineral soil (3.5–4.5), which is unfavourable for soil microorganisms.

Long-term trends in foliage

The foliar concentrations of N were above the critical levels, indicating luxury consumption of N by the trees, while foliar P concentrations were in the lower normal range and sometimes indicated deficiency. The foliar N:P ratio was above the upper critical limit in three plots. Foliar N concentration decreased only in the BRA site, while foliar P concentration, the foliar N:P ratio and the foliar BC:N ratio were unchanged between 1999 and 2013, indicating a nearly stable and unbalanced tree mineral nutrition in the Level II plots. Biotic recovery thus appeared to be lagging behind on the changes in soil solution chemistry. This means that a multiple indicator approach (monitoring of tree

nutritional status alongside soil processes) is needed to monitor the evolution of temperate forest N status. When recovery from acidification results in pH rising above the Al buffer range in decades to come, sudden changes in soil solution Al and in connected availability of P and other nutrients (K, Mg, Ca, ...) may take place with, however, at present unpredictable biotic responses.

Conclusions

Long-term monitoring data collected in five Flemish Level II plots indicated that abiotic N status started to improve and acidification slowed down during the past two decades, due to a sharp decrease in non-marine SO_4^{2-} and NH_4^+ depositions. However, inorganic N depositions are still far above the critical loads for ectomycorrhizal fungi and epiphytic lichens and in the coniferous plots also for ground vegetation. Given the still very low soil pH (3.5–4.5) unfavourable for microbial life, the generally observed tendency of increased DOC and DON mobility is likely a direct result of lowered ionic strength and partly rise in pH, both due to lowered acidifying deposition. Abiotic recovery is delayed by a simultaneous decrease in BC depositions and SO_4^{2-} desorption. Biotic recovery is lagging behind on the changes in soil solution chemistry, as indicated by the stable but unbalanced tree mineral nutrition. More knowledge and data are needed on the air concentrations of intermediate oxidized N compounds. The results from this thesis indicate that the Programmatic Approach to Nitrogen (PAS) is partly missing its target for oxidized N compounds and that extra measures will be necessary to bring NO_x emissions at an acceptable level.

SAMENVATTING

Achtergrond

Verhoogde atmosferische deposities van niet-marien SO_4^{2-} en anorganische N als gevolg van luchtvervuilende emissies veroorzaakten een progressieve verzuring en eutrofiëring met N van bosecosystemen in Europa sinds de start van de industriële revolutie. Verschillende studies wezen uit dat ook Vlaamse bosbodems tussen 1950 en 2000 in toenemend tempo zijn verzuurd en duidelijke tekenen vertoonden van N-verzadiging. Sinds de jaren 1980 werden internationale protocols geïmplementeerd om de emissies van SO_2 te reduceren (1985 Helsinki protocol, 1994 Oslo protocol) en later ook voor anorganische N (1998 Sofia protocol, 1999 Gothenburg multi-pollutant protocol). Dit resulteerde in een algemene scherpe daling van de niet-mariene SO_4^{2-} deposities in Europese bossen. Stikstofdeposities zijn minder sterk gedaald en alleen in regio's met hoge deposities, vooral in centraal NW-Europa. In een aantal lange termijn monitoring plots in bossen waar de verzurende deposities sterk afnamen werd recent een daling van de snelheid van verzuring vastgesteld, terwijl voor N-verzadiging uiteenlopende resultaten werden gevonden, variërend van een beginnend herstel tot verergering van de toestand. Het is onduidelijk in welke mate Europese bossen kunnen herstellen van verzuring en N-verzadiging en hoe lang dit zal duren.

Doelstelling

De eerste doelstelling van deze thesis was het evalueren van de evolutie van atmosferische deposities van niet marien SO_4^{2-} en anorganische N in Vlaamse bossen tijdens de voorbije decennia. Tweede doelstelling was het evalueren van de impact op de chemische bodem(water)kwaliteit in Vlaamse bossen. De uiteindelijke doelstelling was om na te gaan of de snelheid van verzuring en N-verzadiging afneemt en of er al beginnend herstel optreedt.

Deze thesis bundelt een aantal resultaten van het meetnet intensieve monitoring bosecosystemen (Level II) in Vlaanderen. Het Level II meetnet werd officieel opgericht in 1994 door het International Co-Operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests, www.icp-forests.net). De langetermijndata van atmosferische deposities, elementconcentraties in de bodemoplossing en minerale

voedingstoestand van de bomen in vijf Level II plots vormden de basis van het onderzoek voorgesteld in deze thesis.

Depositietrends

Tussen 1994 en 2010 daalde de jaarlijkse TF van ACID in de vijf Level II proefvlakken met 45–74%. Dit is in belangrijke mate te danken aan de daling van de TF van niet-marien SO_4^{2-} met 56–68% en van de TF van NH_4^+ met 40–59%, Parallel is ook de TF van BC gedaald met 19–41%, wat de afname van de TF van ACID (45–74%) enigszins vertraagde. Ongunstig is de trend van de TF van NO_3^-, die na een aanvankelijke daling in 1994–1996 quasi stabiel is gebleven. Actueel zijn de N-deposities nog steeds hoger dan de kritische lastenrange voor vegetatie en gevoelige ectomycorrhiza in verschillende proefvlakken, en bedragen ze een veelvoud van de kritische last voor gevoelige epifytische korstmossen.

De daling van de TF van niet-marien SO_4^{2-} is te verklaren door emissiebeperkende maatregelen in de industrie (SO_2), waaronder de introductie van zwavelarme brandstoffen. Voor de daling van de TF van NH_4^+ leverde vooral de landbouw een bijdrage door het beperken van de NH_3-emissies van stallen en bij het transport en uitrijden van mest (introductie van mestinjectietechnieken). De daling van de NH_4^+-deposities is echter wellicht ook gedeeltelijk toe te schrijven aan een verminderde co-depositie met SO_4^{2-}. De stagnatie van de NO_3^- deposities sinds 1996 kan wellicht verklaard worden door een onderschatting van de NO_x-emissies door het verkeer, rekening houdend met het feit dat voertuigen met een dieselmotor (61% van het wagenpark in 2015) op de weg 6–7 keer meer NO_x uitstoten dan wat standaard labotesten doen uitschijnen (het "dieselgate" schandaal). Er zijn echter nauwelijks gegevens beschikbaar over de verschillende intermediaire geoxideerde N-verbindingen (N_2O_5, HNO_3, HNO_2, PAN en partikel-NO_3^-) in de atmosfeer, wat het moeilijk maakt om de link te leggen tussen NO_x-emissies en NO_3^--deposities in Vlaamse bossen.

De huidige Programmatische Aanpak Stikstof (PAS) van de Vlaamse overheid onder de EU Habitatrichtlijn ([https://www.natura2000.vlaanderen.be/pas)](https://www.natura2000.vlaanderen.be/pas) werd gelanceerd met de bedoeling om de N-emissies verder te reduceren, maar is hoofdzakelijk gefocust op het verder terugdringen van de NH_3-emissies door de landbouwsector. Rekening houdend met de stagnerende BD en TF van NO_3^- in de Level II proefvlakken is het BAU2030-

scenario wellicht te optimistisch, wat suggereert dat de PAS-maatregelen niet zullen volstaan om Natura 2000 boshabitats tegen 2050 voldoende te beschermen.

Trends in de bodemoplossing

De daling van de verzurende en vermestende deposities tussen 1994 en 2010 ing gepaard met een gelijktijdige daling van de ionenconcentraties in de bodemoplossing (NO_3^-, Al_{tot}, SO_4^{2-} and BC) in de vijf Level II proefvlakken. De pH van de bodemoplossing vertoonde tot 2004 nog een licht neerwaartse trend, nam tijdens de laatste 10 jaar met ongeveer 0.5 eenheden toe. De stijgende pH en dalende ionensterkte en Al-concentraties in de bodemoplossing kunnen de toenemende DOC concentraties in de humuslaag en de minerale bodem tussen 2002 en 2012 verklaren. DOC fluxen namen eveneens toe in de humuslaag maar waren vrijwel stabiel in de minerale bodem. Concentraties en fluxen van DON in de bodemoplossing vertoonden gelijkaardige trends als DOC tussen 2005 en 2013. DON bleek mobieler te zijn dan DOC, mogelijk door selectieve re-adsorptie in de minerale bodem. De molaire DON:TDN verhouding (2005–2014) and the molaire DOC:NO_3^- verhouding (2002–2014) vertoonden eveneens toenemende trends. De toename van beide ratio's was gedeeltelijk het resultaat van een toegenomen mobilisatie van DOC en DON en was dus niet volledig indicatief voor een verbetering van de N-status van de bosbodem.

De ANC vertoonde een stijgende trend, maar bleef negatief, wat erop wijst dat de bodemverzuring vertraagt, maar nog steeds verdergaat. Bovendien vertoont de BC:Al_{tot} verhouding in de bodemoplossing een dalende trend, wellicht doordat de uitspoeling van BC onvoldoende gecompenseerd wordt door de input via strooiselomzetting, mineralisatie en de dalende deposities. In de drie Level II proefvlakken op zandige bodem met lage CEC en BS overschrijdt de BC:Altot verhouding nog steeds het kritieke niveau voor schade aan fijne wortels, verhinderde wortelgroei en groeireducties tot 80% van de gemiddelde groei. Het herstel van verzuring werd vertraagd door SO_4^{2-}-desorptie, de gelijktijdige daling van de BC-depositie en mogelijk ook door een stijgende organische zuurheid, zoals aangeduid door de toenemende DOC concentraties in de bodemoplossing.

De waargenomen veranderingen in de bodemoplossing zijn wellicht puur chemisch (abiotisch) van aard, gezien de nog steeds zeer lage pH van de bodemoplossing en pH-

$CaCl_2$ van de minerale bodem (3.5–4.5), die in principe ongunstig is voor micro-organismen.

Trends in de bladconcentraties

De concentraties van N in de bladeren en naalden waren hoger dan de kritische limieten (luxeconsumptie), terwijl de P-concentraties zich in het lage gedeelte van het normale bereik bevonden en in bepaalde gevallen P-gebrek aanduidden. De N:P verhouding was in drie proefvlakken hoger dan de kritische limiet. De N:P verhouding, BC:N verhouding en P-concentraties bleven onveranderd tussen 1999 en 2013, terwijl de N-concentraties alleen in Brasschaat een dalende trend vertoonden, wat wijst op een stabiele, maar onevenwichtige minerale voedingstoestand van de bomen in de Level II plots. Het biotisch herstel bleef dus achter op de chemische veranderingen in de bodemoplossing. Dit betekent dat een multi-indicator benadering (monitoring van processen in de bodem en van de minerale voedingstoestand) vereist is om de evolutie van de N status in gematigde bossen op te volgen. Wanneer herstel van verzuring in de komende decennia resulteert in een toename van de pH van de bodemoplossing boven het Al-bufferbereik, dan kunnen mogelijk plotse veranderingen in de Al-concentraties en beschikbaarheid van P en andere nutriënten (K, Mg, Ca, ...) optreden met momenteel onvoorspelbare biotische reacties.

Conclusies

Langetermijndata verzameld in de vijf Vlaamse Level II proefvlakken tonen aan dat in Vlaamse bossen een beginnend chemisch herstel van N-verzadiging optreedt en dat de verzuring minder snel verloopt dan twee decennia geleden, dankzij een sterke daling van de deposities van niet-marien SO_4^{2-} en NH_4^+. De N-deposities liggen echter nog steeds ver boven de kritische lasten voor ectomycorrhiza en epifytische korstmossen en in de naaldboomproefvlakken ook voor de kruidvegetatie. Gezien de nog steeds zeer lage pH van de bodem (3.5–4.5), wat ongunstig is voor microbieel leven, is de toegenomen mobiliteit van DOC en DON waarschijnlijk een direct gevolg van de gedaalde ionensterkte en deels ook de lichte toename van de pH van de bodemoplossing, beide het gevolg van de afname in verzurende deposities. Het abiotisch herstel wordt vertraagd door een gelijktijdige daling van de deposities van BC, en desorptie van SO_4^{2-}. Het biotisch herstel loopt achter op de veranderingen in de bodemoplossing, wat blijkt uit de vrijwel stabiele, maar onevenwichtige minerale voedingstoestand van de bomen. Meer kennis en data

zijn nodig inzake de concentraties van intermediaire geoxideerde N-verbindingen in de lucht. De resultaten van deze thesis wijzen uit dat de Programmatische Aanpak Stikstof (PAS) deels zijn doelstelling mist voor wat geoxideerde N-verbindingen betreft en dat extra maatregelen nodig zullen zijn om de NO_x-emissies naar een aanvaardbaar niveau te brengen.

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CURRICULUM VITAE

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Education

2000–2001	GAS Human Ecology
	Free University of Brussels, Faculty of Medicine and Pharmacy
1998–2000	MSc in Bioscience engineering, Land & Forest Management
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1995–1998	BSc in Bioscience engineering, Land & Forest Management
	Ghent University, Faculty of Agricultural and Applied Biological Sciences
1989–1995	Secondary school (Sciences–Mathematics)
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Professional experience

February 2001–present	Scientist at the Institute for Forestry and Game Management, since 2006 transformed to the Research Institute for Nature and Forest (INBO), Gaverstraat 35, 9500 Geraardsbergen.

Scientific publications

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Scientific activities

Participation in congresses, symposia or workshops

Prescher, A.-K., Schmitz, A., Johnson, J., Vanguelova, E., Cools, N., Gottardini, E., Nieminen, T.M., Schaub, M., Ukonmaanaho, L., Verstraeten, A., Waldner, P. and Seidling, W. Change in Sulphur pools in forest ecosystems following the reduction of atmospheric SO_2 – First steps. IUFRO 125th Anniversary Congress 2017, 18-22 September 2017, Freiburg, Germany. (oral presentation)

Schmitz, A., Hansen, K., Michel, A., Prescher, A.-K., Sanders, T.G., Seidling, W., Clarke, N., Verstraeten, A., Pihl Karlsson, G., Zlindra, D., Vesterdal, L., Benham, S., Elustondo, D., Nicholas, M. and Waldner, P. Inorganic nitrogen deposition to forest ecosystems in Europe - Spatial patterns and temporal changes in the past 15 years. IUFRO 125th Anniversary Congress 2017, 18-22 September 2017, Freiburg, Germany. (oral presentation)

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Verstraeten, A. Pollen distribution causes the spring peak in throughfall dissolved organic carbon (DOC) in beech (Fagus sylvatica L.) / common oak (Quercus robur L.) forests. ICP Forests 33rd Task Force meeting, 17-19 May 2017, Bucharest, Romania. (oral presentation)

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