Dynamics and effects of nitrogen in European forest ecosystems

Dissertation to attain the doctoral degree (Dr. forest.)
of the Faculty of Forest Sciences and Forest Ecology
Georg-August-University Göttingen

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Recklinghausen, April 2023

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Date of oral examination: 2023-06-26

Summary

Anthropogenic nitrogen (N) emissions drastically altered the global N cycle over the 20th century. Activities associated with N emissions, such as intensive agriculture and the burning of fossil fuels, greatly increased human well-being. At the same time, the numerous environmental impacts of elevated N availability became apparent. In Europe, N deposition decreased by 36% between 1990 and 2018 due to clean air policies and economic transformation but is in many regions still at a high level. Europe's forests are an important receptor for N emissions, due to their large land use share and efficient filtering of air pollutants by the tree canopies. An understanding of the responses of forest ecosystems to the decrease in N deposition is important for an effects-based monitoring of clean air policies as well as from a forest ecology perspective. While previous studies reported on specific aspects and areas, the first part of this dissertation provides a European perspective, covering responses to decreasing N deposition of several forest ecosystem parameters. In addition to understanding the responses of forests to N deposition, quantifying the magnitude of N inputs to forests remained challenging, because particulate and gaseous N deposition on the canopies is difficult to measure directly. However, the enforcement of clean air policy and the development of nutrient-sustainable forest management strategies require reliable data on atmospheric deposition. Therefore, the second and third part of this dissertation focus on uncertainties in commonly used methods for calculating N deposition with respect to potential improvements of accuracy.

In the first study, we addressed the question of whether Europe's forest ecosystems have already responded to the decrease in N deposition since the 1990s. We reviewed observational and experimental studies covering the domains of soil acidification and eutrophication, understory vegetation, tree nutrition (foliar element concentrations), tree vitality, and tree growth. Results were generally very heterogeneous, likely linked to the spatial heterogeneity in levels and trends of N deposition across Europe. For soil solution nitrate concentrations, we found moderate indication for a response (decrease), likely related to the reduction of N deposition. For tree nutrition (foliar N concentrations), several studies reported negative (decreasing) trends for beech, oak, and some for spruce. Further research is required to clarify whether this trend is caused by the reduction of N deposition or by an increase in foliar mass due to rising atmospheric CO_2 concentrations ("dilution effect"). Several studies report increasing nutrient imbalances (e.g. N:P), which highlights the necessity for incorporating aspects of nutrient sustainability into the planning of biomass removal from forests. We did not find an indication of a large-scale response of understory vegetation, tree growth, or tree vitality to the decrease of N deposition in Europe. Both observational and experimental studies

suggest that some forest ecosystem parameters react faster (e.g. soil solution), some slower (e.g. understory vegetation) to changes in N supply. Current and expected future levels of emission reduction are likely insufficient to cause widespread responses.

In a second study, we addressed the question to what extent N deposition estimates from large-scale spatial models (“emission-based method” EBM) match with in-situ measurements of N deposition. EBM data is regularly required for the enforcement of clean air policy, for example in licensing procedures for N-emitting facilities. Using Germany as a case study, we compared N deposition estimates from the EBM provided by the German Environment Agency to estimates from two methods based on local measurements at around 100 German intensive forest monitoring stations (“canopy budget model” CBM and “inferential method” IFM). We found that in-situ measurements yield on average 2 $\mathrm{kg\ N\ ha^{-1}\ a^{-1}}$ (CBM) to 6 $\mathrm{kg\ N\ ha^{-1}\ a^{-1}}$ (IFM) higher N deposition rates compared to the EBM (average deposition rate at the German intensive forest monitoring stations according to the EBM is 18 $\mathrm{kg\ N\ ha^{-1}\ a^{-1}}$). While a good agreement was found for wet deposition (WD), the EBM provided lower dry deposition (DD) estimates at stronger polluted plots. Differences were most pronounced at spruce plots and partly linked to meteorological variables. Further reductions of the uncertainty inherent in all three methods are required to provide reliable information for clean air policy and forest management decisions.

In a third study, we covered one aspect of uncertainty in the CBM method. Specifically, we examined the assumption that the potassium-to-sodium ratios (K^+:Na^+) in WD and DD are equal. Due to the lack of long-term direct DD measurements for forests, we simulated the DD of K^+ (DD_K) and Na^+ (DD_{Na}) with a process-oriented model. Simulations were performed based on six years of daily $PM_{2.5}$ and PM_{10} measurements at the air quality monitoring station “Melpitz" in rural Germany. We found that the average K^+:Na^+ ratio in simulated DD was 0.4 - 0.43 (depending on assumed forest receptor properties). This exceeded the K^+:Na^+ ratio in WD measured at the Melpitz station (0.24) by a correction factor of 1.66 - 1.77. Due to uncertainties in the DD simulation approach, we consider our results as an indication, but not evidence, for an underestimation of DD_K by the CBM. Applying the correction factors at five intensive forest monitoring plots in the same region as the Melpitz station did not result in relevant changes in the calculated N deposition (maximum change in N deposition: 2%). We conclude that the simplifying assumption of similar substance ratios in DD and WD underlying the CBM was potentially relevant in the context of nutrient sustainability (K^+ deposition rates), but not for the calculation of N deposition. Further research is required to test whether these results generalize to regions with different atmospheric conditions.

Zusammenfassung

Anthropogene Emissionen von Stickstoff (N) haben im 20. Jahrhundert zu einer deutlichen Veränderung des globalen N-Kreislaufs geführt. Die mit der N-Freisetzung verbundenen Aktivitäten, wie die Intensivlandwirtschaft und die Verbrennung fossiler Energieträger, haben die Lebensqualität für einen erheblichen Teil der Weltbevölkerung gesteigert. Zugleich wurden jedoch auch negative Effekte der N-Emissionen deutlich. In Europa sind die N-Einträge im Zeitraum 1990 bis 2018 infolge von Luftreinhaltemaßnahmen und ökonomischem Wandel um etwa 36% gesunken, befinden sich aber in vielen Regionen weiterhin auf einem hohen Niveau. Dabei sind Wälder aufgrund des großen Flächenanteils und der effizienten Filterwirkung der Baumkronen für Luftschadstoffe ein wesentlicher Rezeptor für die N-Belastung. Ein Verständnis der Folgen des Rückgangs der N-Einträge für die Wälder Europas ist als wirkungsseitige Erfolgskontrolle der Luftreinhaltepolitiken und aus waldökologischer Perspektive bedeutsam. Während bisherige Studien Information zu einzelnen Aspekten dieser Fragestellung bereitstellen, liefert der erste Teil der vorliegenden Dissertation eine europäische Gesamtschau über mehrere Wirkungsbereiche. Neben der Erfassung der Auswirkungen stellt auch die Quantifizierung der Höhe der N-Einträge eine Herausforderung dar, weil die Messung der partikulären und gasförmigen Deposition in den Kronenraum methodisch sehr aufwändig ist. Für die Umsetzung von Luftreinhaltemaßnahmen und die Entwicklung nährstoffnachhaltiger Waldbewirtschaftungsstrategien ist die korrekte Erfassung der atmosphärischen Deposition jedoch von großer Bedeutung. Der zweite und dritte Teil der vorliegenden Dissertation adressieren daher Unsicherheiten in den derzeit genutzten Methoden zur Quantifizierung der N-Einträge im Hinblick auf Verbesserungsmöglichkeiten.

In einer ersten Studie wurde die Frage bearbeitet, wie die Waldökosysteme Europas auf den Rückgang der N-Einträge seit etwa 1990 reagiert haben. Dazu wurde eine Literaturauswertung von Beobachtungsstudien zu den Themenbereichen Versauerung und Eutrophierung des Waldbodens, Bodenvegetation, Baumernährung, Waldzustand und Waldwachstum durchgeführt. Ein wesentliches Merkmal der untersuchten Studien war die große Heterogenität der Reaktionen auf die rückläufigen N-Einträge in Europa. Chemische Analysen der Bodenlösung unter Wald deuten auf einen moderaten Rückgang der Nitratkonzentrationen hin, was vermutlich eine Reaktion auf die rückläufigen N-Einträge darstellt. Beobachtungsstudien zur Baumernährung berichten von einem leichten Rückgang der N-Konzentrationen in den Blättern/Nadeln für Buche, Eiche und z.T. auch Fichte. Ob der Rückgang der N-Deposition oder eine Zunahme der Blatt/-Nadelmasse infolge des Anstiegs der atmosphärischen CO_2-Konzentrationen („Verdünnungseffekt“) für diese Entwicklung

ursächlich ist, lässt sich zum aktuellen Zeitpunkt nicht abschließend klären. Die vielfach berichtete Zunahme von Nährstoffungleichgewichten (z.B. N:P) verdeutlicht die Notwendigkeit, Aspekte der Nährstoffnachhaltigkeit bei der Biomasseentnahme zu berücksichtigen. Bezüglich der Bereiche Bodenvegetation, Waldwachstum und Waldzustand wurden keine Studien gefunden, die von großräumigen Reaktionen auf den Rückgang der N-Einträge in Europa berichten. Sowohl Beobachtungsstudien als auch experimentelle Studien deuten darauf hin, dass einige Untersuchungsbereiche schneller (z.B. Bodenlösung) und andere langsamer (z.B. Bodenvegetation) auf eine Verringerung der N-Einträge reagieren. Die Größenordnung der bisherigen und zukünftig erwartbaren Rückgänge der N-Einträge in die Wälder Europas ist wahrscheinlich nicht ausreichend, um großskalige Reaktionen in allen Untersuchungsbereichen hervorzurufen.

In einer zweiten Studie wurde die Frage bearbeitet, in wie weit großskalige räumlich aufgelöste Modelle („emissionsbasierte Methode“, EBM) hinsichtlich der N-Deposition mit in-situ Messungen übereinstimmen. EBM-Daten werden routinemäßige für die Umsetzung von Luftreinhaltepolitiken herangezogen, beispielsweise im Kontext von Genehmigungsverfahren für N-emittierende Anlagen. Am Beispiel des vom Umweltbundesamt bereitgestellten EBM-Datensatzes wurde ein Vergleich der N-Depositionsraten mit zwei auf lokalen Messungen basierenden Verfahren (“Kronenraumbilanzmodell” KRB und “Inferentialmethode” IFM) an etwa 100 forstlichen Intensivmonitoringflächen in Deutschland durchgeführt. Die auf den in-situ Messdaten basierenden Methoden lieferten im Mittel 2 $\mathrm{kg\,N\,ha^{-1}\,a^{-1}}$ (KRB) bis 6 $\mathrm{kg\,N\,ha^{-1}\,a^{-1}}$ (IFM) höhere N-Depositionsraten verglichen mit der EBM. Die mittlere N-Depositionsrate an den Intensivmonitoringflächen entsprechend der EBM lag bei 18 $\mathrm{kg\,N\,ha^{-1}\,a^{-1}}$. Während eine gute Übereinstimmung bezüglich der nassen Deposition (WD) gefunden wurde, liefert die EBM insbesondere bei stärker belasteten Standorten geringere Trockendepositionsraten (DD) als die KRB und die IFM. Der Unterschied zwischen den Methoden war an Fichtenflächen besonders ausgeprägt und hing teilweise mit meteorologischen Größen zusammen. Um eine belastbare Datengrundlage für Luftreinhaltemaßnahmen und Waldbewirtschaftungsstrategien bereitzustellen, ist eine Verringerung der erheblichen Unsicherheiten erforderlich, mit der alle verglichenen Methoden behaftet sind.

In einer dritten Studie wurde ein spezifischer Aspekt der Unsicherheit in der KRB-Methode untersucht. Es wurde die Annahme überprüft, dass die Kalium-Natrium-Verhältnisse (K^+:Na^+) in der WD und der DD ähnlich sind. Aufgrund des Mangels an direkten Messungen der DD in Wälder über längere Zeiträume wurde die DD von K^+ (DD_K) und Na^+ (DD_{Na}) mit einem prozessorientierten Modell simuliert. Als Datengrundlage dienten sechs Jahre täglicher Konzentrationsmessungen in zwei Größenklassen ($PM_{2.5}$ und PM_{10}) an der Luftqualitäts-Messstation „Melpitz" bei Leipzig. Das mittlere K^+:Na^+-Verhältnis in der (simulierten) DD war 0.4 - 0.43 (abhängig von den angenommenen Rezeptoreigenschaften der Waldbestände), während das K^+:Na^+-Verhältnis der in Melpitz gemessenen WD im Mittel bei 0.24 lag. Damit müsste die DD_K entsprechend des KRB-Ansatzes mit einem Korrekturfaktor von 1.66 - 1.77 multipliziert werden, um die DD_K des prozessorientierten DD-Modells zu erreichen. Aufgrund der Unsicherheiten in dem genutzten Simulationsansatz werden die Ergebnisse als möglicher Hinweis aber nicht als eindeutiger Befund einer Unterschätzung von DD_K durch die KRB interpretiert. Die Anwendung dieser Korrekturfaktoren an fünf Intensivmonitoringflächen in derselben Region wie Melpitz führte nicht zu einer nennenswerten Änderung der mit der KRB berechneten N-Deposition (größte Abweichung: 2%). Die vereinfachende Annahme ähnlicher Substanzverhältnisse in der DD und WD, die der KRB-Berechnung zugrunde liegt, war somit potentiell problematisch für Betrachtungen zur Nährstoffnachhaltigkeit (Höhe der K^+-Einträge), aber nicht für die Berechnung der Höhe der N-Deposition. Weitere Untersuchungen sind erforderlich, um zu überprüfen, ob diese Ergebnisse auf Regionen mit anderen atmosphärischen Bedingungen übertragbar sind.

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1. General Introduction

1.1 Human interventions in the global nitrogen cycle

The industrial-scale conversion of inert atmospheric nitrogen to reactive nitrogen (N) has been termed "the greatest single experiment ever made in geoengineering" (Sutton et al., 2011). Made possible by the development of the Haber-Bosch process at the beginning of the 20th century, it solved the problem of limited natural N sources (Erisman et al., 2011). Total annual anthropogenic N production, including N from the Haber-Bosch process, fossil fuel combustion, and legume cultivation, has exceeded the rate of natural terrestrial N fixation in the second half of the 20th century (UNEP and WHRC, 2007). The global N cycle is considered (together with phosphorus) one of the nine planetary boundaries defining the environmental limits in which humanity can safely operate. Its status is currently considered in the worst category ("beyond the zone of uncertainty - high risk") (Steffen et al., 2015).

The massive anthropogenic intervention in the global N cycle is driven by the many benefits associated with activities involving the release of N to the environment. Most importantly, the Haber-Bosch process lays the foundation for intensive agriculture and is responsible for feeding around half of the world's population (Erisman et al., 2008). The provision of goods and services in the context of transportation, industrial processes, and energy generation often involves the combustion of fossil fuels with the corresponding release of N to the atmosphere. The large-scale anthropogenic N emissions also have a range of unintended consequences with huge associated costs. These include a reduction of air quality by N compounds (either directly or as precursor substances) with negative effects on human health (Gowers et al., 2020; Huang et al., 2021), aggravation of climate change (IPCC, 2022), pollution of drinking water (Ward et al., 2018) as well as a cascade of effects on terrestrial, freshwater and marine ecosystems (De Vries, 2021; Galloway et al., 2003). Nitrogen pollution is among the most important threats to global biodiversity (Bobbink et al., 2010; Clark et al., 2013). Solutions to this problem are suggested at different spatial and political levels, including efforts by the United Nations Environment Programme (UNEP) toward the establishment of an International Nitrogen Management System (INMS) (Sutton et al., 2019).

1.2 Nitrogen in Europe's Forests

In Europe, N emissions are regulated by international frameworks like the Convention on Long-Range Transboundary Air Pollution (CLRTAP) under the United Nations Economic Commission for Europe (UNECE) or by the National Emission Reduction Commitments Directive (NECD) under the EU (Wettestad, 2017). Clean air policy and economic transformation achieved a 36% reduction in N deposition to EU28+ territory between 1990 and 2018, but N deposition remains at a high level (Engardt et al., 2017). For example, the critical load for N deposition was exceeded on 62% of the ecosystem area in Europe in 2015 (Slootweg et al., 2015). “Critical load” refers to '*a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge*' (Nilsson and Grennfelt, 1988). Europe's forests are a large receptor for anthropogenic N emissions as they cover 35% of the total land area (FOREST EUROPE, 2020) and because forest canopies filter many gaseous and particulate air pollutants more effectively than other land use types (Fowler et al., 1989).

N in Europe's forests has a variety of effects, including a shift in understory plant species composition towards more nitrophilous species (van Dobben and De Vries, 2017), negative impacts on macrolichens (Giordani et al., 2014) and ectomycorrhizal fungi (van der Linde et al., 2018). Furthermore, N deposition increases the risk of nitrate leaching (Dise and Wright, 1995; Gundersen et al., 1998) and contributes to the acid load in forest soils that is still present from past decades of high sulfur deposition (Fleck et al., 2019). At the same time, N deposition has been found to stimulate tree growth in large parts of Europe (Etzold et al., 2020; Kahle, 2008) and nitrogen fertilization of forests is conducted in some regions with low N deposition (Lindkvist et al., 2011). In addition to these effects, N deposition in Europe affects tree mineral nutrition (Sardans et al., 2015). While originally evolved under pre-industrial conditions where N was a main limiting resource, tree species' foliar N status is nowadays in the “surplus” range for some tree species and regions. For example, the second National Forest Soil Inventory in Germany (2006 - 2008) found that foliar N concentrations were in the “surplus” range for more than 50% of Scots pine (n = 180) and oak (n = 124) plots (Talkner et al., 2019). On the other hand, there is an ongoing discussion about indications for a decreasing foliar N nutrition (De Vries and Du, 2022; Mason et al., 2022; Penuelas et al., 2020). For example more than 50% of the Norway spruce plots within the pan-European forest monitoring network “ICP Forests” had foliar N concentrations in the “deficiency” range (Jonard et al., 2015; Sanders et al., 2017). In addition, the availability of nutrients other than N, especially phosphorus, is deteriorating in Europe (Jonard et al., 2015; Talkner et al., 2015).

1.3 Research needs

Considering the various costs and benefits of human activities associated with N emissions, decision makers require up-to-date information on the effects of changes in N deposition regimes. This applies to policy design in the context of clean air regulations as well as to forest managers regarding nutrient sustainability, tree growth, and forest health. However, effects-based research so far mainly focused on how elevated N deposition impacts ecosystems, for example summarized by Bobbink and Hettelingh (2011) and Bobbink et al. (2022). In contrast, the question how forest ecosystems react to a reduction of N deposition has received less attention so far. First indications arose from experiments at several forest sites in Europe, where N inputs were artificially decreased by roofing (Wright and Rasmussen, 1998) or N inputs decreased back to ambient levels after a temporary artificial increase (Strengbom et al., 2001). Observational studies on trends in forest ecosystem parameters started to address the question of responses to decreasing N deposition (Stevens, 2016; Verstraeten et al., 2017), but an overview of the current state of knowledge on the responses of forest ecosystems in Europe to decreasing N deposition is still lacking.

While effects-based research provides the information necessary for policy design, executive authorities at various administrative levels must enforce existing N management regulations. This applies for example to licensing procedures for N-emitting projects like agricultural facilities, road construction, or power plants. In this context, expected additional N deposition from planned projects is typically added on top of a static "background deposition" map to assess the exceedance of threshold values for N deposition to protected habitats. Corresponding background deposition maps are often based on chemical transport models ("emission-based method" EBM) and made available for the administration and general public for example in the Netherlands (e.g. Heer et al. 2017), Switzerland (BAFU, 2020; Rihm and Künzle, 2019) and Germany (Schaap et al., 2018). EBM results can be easily validated against measurements of wet deposition (WD, mainly rain and snow), as these measurements are relatively widely available. In contrast, validation of N deposition maps for land cover types (like forests) with a larger share of dry deposition (DD) is more challenging. This is because tree canopies effectively filter particles and gases from the atmosphere, which is hard to measure directly. Precise measurements of DD to forests are costly and thus limited to short time periods and single sites (Wintjen et al., 2022). More widely available but less accurate "ground truthing" data comes from currently around 300 ICP Forests intensive forest monitoring stations (Marchetto et al., 2022). N deposition to forests is not measured directly in this monitoring network, but can be calculated either using the "canopy budget model" (CBM) approach (based on precipitation measurements under the forest canopy (stand deposition) and at a nearby open field site), or according to the “inferential method” (IFM, based on locally measured air concentration data). Examples for cross-validating background deposition maps against data derived from in-situ measurements include a study by Karlsson et al. (2019). They compared EBM data from the Swedish National Environmental Monitoring Programme with a modified CBM approach calculated at intensive forest monitoring sites, which was supplemented with additional measurements of substance ratios in DD. In another study, Thimonier et al. (2019) compared EBM-based deposition estimates for Switzerland against data from intensive forest monitoring stations using the IFM approach and a strongly simplified CBM approach. A comparison of N and S deposition from a Europe-wide EBM (the EMEP MSC-W model) with ICP Forests data has been conducted by Simpson et al. (2006) and Marchetto et al. (2021). Although they included many monitoring sites, the interpretability of their results for N deposition was limited because they used the stand deposition measurements directly, without calculating atmospheric N deposition with a CBM or IFM approach. While cross-validation studies between EBM data and in-situ measurements were conducted for some European countries, a corresponding comparison of the German background N deposition map with data from intensive forest monitoring sites is missing so far (but see Schaap et al. (2018) for a first attempt).

Cross-validation of N deposition estimates from different methods is important to characterize methodological uncertainty and highlight potentials for improvement. In the case of the CBM approach, uncertainty results from several nested assumptions required during the calculation steps (Adriaenssens et al., 2013; Thimonier et al., 2019). These assumptions include the canopy-inertness of the “tracer substance”, similarity of substance ratios in DD and WD as well as numerical values for parameters quantifying the exchange of N against other substances in the tree canopies. So far, only very limited efforts were undertaken to validate these assumptions (Draaijers et al., 1997; Mohr et al., 2005; Thimonier et al., 2008). The assumption of similar potassium-to-sodium (K^+:Na^+) ratios in DD and WD is especially debated, as these substances typically occur in particles with different sizes (Adriaenssens, 2012). The unquantified uncertainties of the CBM approach are a major obstacle to the wider use of deposition measurements continuously collected at intensive forest monitoring sites across Europe as ground-truthing data for researchers and policy makers.

1.4 Objectives and approaches

Given the challenges outlined above, this dissertation addresses three objectives:

1. Provide an overview of the responses of forest ecosystems in Europe to the decrease in N deposition that occurred in the last decades.
2. Provide a comparison of the background N deposition map from the German Environment Agency against in-situ measurements at forest monitoring stations.
3. Quantify the uncertainty in CBM-based N deposition estimates resulting from the assumption of similar K^+:Na^+ ratios in wet and dry deposition.

To address the first objective, we reviewed observational studies from across Europe for responses of forest ecosystems to decreasing N deposition, covering the domains of soil acidification and eutrophication, understory vegetation, tree nutrition (foliar element concentrations), tree vitality, and tree growth. We complemented the results from observational studies with findings from experimental studies. For the second objective, we compared the background N deposition map provided by the German Environment Agency to N deposition estimates based on measurements at around 100 forest monitoring stations in Germany. For the third question, we simulated the DD of K^+ and Na^+ with a process-oriented model based on six years of $PM_{2.5}$ and PM_{10} data at a rural monitoring station in Germany. We quantified by how much CBM-based DD estimates of K^+ would need to be corrected to match the K^+ DD from the process-oriented model. In a final step, we applied these corrections to CBM calculations at five intensive monitoring sites in the same region and analyzed how this affects CBM-based N deposition estimates.

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2. Responses of forest ecosystems in Europe to decreasing nitrogen deposition

Schmitz, A.; Sanders, T. G. M.; Bolte, A.; Bussotti, F.; Dirnböck, T.; Johnson, J.; Peñuelas, J.; Pollastrini, M.; Prescher, A.-K.; Sardans, J.; Verstraeten, A.; de Vries, W.

Published Journal Article, *Environmental Pollution* 2019, *244*, 980–994.

https://doi.org/10.1016/j.envpol.2018.09.101

Environmental Pollution 244 (2019) 980–994

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Responses of forest ecosystems in Europe to decreasing nitrogen deposition☆

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ARTICLE INFO

Article history:
Received 15 June 2018
Received in revised form
17 September 2018
Accepted 20 September 2018
Available online 26 October 2018

Keywords:
Nitrogen deposition
Forest monitoring
Emission reduction
Recovery
Air pollution

ABSTRACT

Average nitrogen (N) deposition across Europe has declined since the 1990s. This resulted in decreased N inputs to forest ecosystems especially in Central and Western Europe where deposition levels are highest. While the impact of atmospheric N deposition on forests has been receiving much attention for decades, ecosystem responses to the decline in N inputs received less attention. Here, we review observational studies reporting on trends in a number of indicators: soil acidification and eutrophication, understory vegetation, tree nutrition (foliar element concentrations) as well as tree vitality and growth in response to decreasing N deposition across Europe. Ecosystem responses varied with limited decrease in soil solution nitrate concentrations and potentially also foliar N concentrations. There was no large-scale response in understory vegetation, tree growth, or vitality. Experimental studies support the observation of a more distinct reaction of soil solution and foliar element concentrations to changes in N supply compared to the three other parameters. According to the most likely scenarios, further decrease of N deposition will be limited. We hypothesize that this expected decline will not cause major responses of the parameters analysed in this study. Instead, future changes might be more strongly controlled by the development of N pools accumulated within forest soils, affected by climate change and forest management.

1. Introduction

Anthropogenic emissions drastically altered the global nitrogen (N) cycle (Fowler et al., 2013; Galloway et al., 2003; Vitousek et al., 1997), with human activities becoming the dominant contribution to the annual release of reactive N to the atmosphere (Fowler et al., 2015; Galloway et al., 2004). The increase in anthropogenic emissions arose from accelerated fossil fuel burning since the industrial revolution, the advent of the Haber-Bosch process to create reactive N from inert atmospheric N_2 at the start of the 20th century as well as an increase in mass transportation and livestock numbers

☆ This paper has been recommended for acceptance by Enzai Du.

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https://doi.org/10.1016/j.envpol.2018.09.101
0269-7491/

(Engardt et al., 2017; Erisman et al., 2011). Today, 18% of the global anthropogenic nitrogen fixation can be attributed to combustion processes, 55% to fertilizer production, and 27% to biological N fixation in agriculture (Fowler et al., 2015). These activities have created benefits, such as the support of human nutrition by mineral fertilizers (Erisman et al., 2008). On the other hand, the release of reactive N causes considerable damages to human health (Van Grinsven et al., 2013) and induces changes in natural and semi-natural ecosystems, such as N deposition being one of the greatest threats to global plant diversity (Bobbink et al., 2010; Brink et al., 2011; Clark et al., 2013; Erisman et al., 2008; Soons et al., 2017; Vitousek et al., 1997).

In Europe N emissions and corresponding deposition increased from pre-industrial times till the mid-1980s, followed by a decrease since the 1990s (Engardt et al., 2017). The decline in N emissions is due to a combination of emission abatement policies and economic transformation (Erisman et al., 2003). In Europe's forests, N deposition caused a variety of changes, including impacts on tree productivity (De Vries et al., 2017b, 2006; Kahle, 2008), tree nutrition reflected in foliar concentrations (Jonard et al., 2015; Sardans et al., 2016b; Waldner et al., 2015), sensitivity of trees to biotic and abiotic stress (Bobbink and Hettelingh, 2011), the composition of understory vegetation (Dirnböck et al., 2014; van Dobben and De Vries, 2017) and ectomycorrhizal fungal communities (van der Linde et al., 2018), to soil chemistry, and increased leaching of N from forest soils to surface and ground waters (Dise et al., 2009; Gundersen et al., 2006). In recent decades, much discussion took place to identify the mechanisms as well as the time frame by which forest ecosystems are impacted by elevated nitrogen deposition. The concept of *nitrogen saturation* (Aber et al., 1998, 1989; Ågren and Bosatta, 1988; De Vries and Schulte-Uebbing, 2018; Lovett and Goodale, 2011) suggests a set of reactions including loss of plant species diversity, N losses with seepage water, soil acidification, and growth reduction. A recent perspective on the stages of N saturation is depicted in Fig. 1. Ecological understanding is used to determine critical loads of N deposition defined as '*a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge*' (Nilsson and Grennfelt, 1988). Critical loads underpin emission protocols at the European scale such as the Revised National Emissions Ceilings Directive (NECD) and are also applied for example in North America (Pardo et al., 2011; Schindler and Lee, 2010) and Asia (Duan et al., 2016). Exceedances of critical loads indicate risks of adverse effects on various aspects of forests, such as tree nutrition and forest biodiversity (De Vries et al., 2015; Nordin et al., 2005; Waldner et al., 2015).

A large part of the ecological research in this context focused on the responses of forest ecosystems to elevated N deposition resulting in N saturation or the exceedance of critical loads. However, much less attention was paid to the potential dynamics of a "recovery" from high N loads although a decline of N deposition to Europe can be observed since the 1990s. The average deposition of inorganic N across all land-use types in Europe decreased from 10.3 kg N ha^{-1} a^{-1} in 1990 to 6.6 kg N ha^{-1} a^{-1} in 2018 (after Engardt et al. (2017), data kindly provided by Magnuz Engardt and David Simpson). The trends are distributed heterogeneously in space. While many forests in areas with higher absolute levels of N deposition (e.g. in Central and Western Europe) experienced a decrease in N inputs, less clear trends have been reported for Northern Scandinavia and parts of Southern Europe (Figs. 2 and 3). Note that despite these reductions, 62% of the European ecosystem area was at risk of eutrophication due to the exceedance of the critical load for eutrophication in 2015 (Slootweg et al., 2015).

This study addresses the response of European forest ecosystems to decreasing N deposition. We review published results from observational and experimental studies on well-monitored parameters: soil acidification and eutrophication, foliar chemistry, ground vegetation composition, tree vitality, and tree growth. This set of indictors covers a range between *endpoint metrics*, i.e. aspects

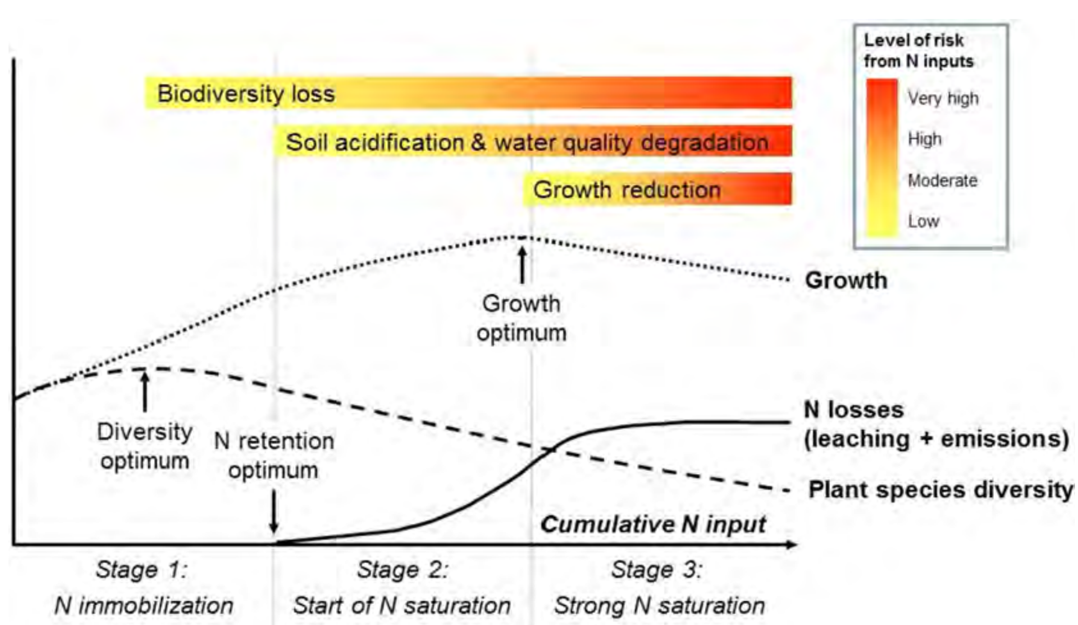

Fig. 1. Hypothetical relationship between the stage of nitrogen saturation and the effects on terrestrial ecosystems in terms of soil processes, vegetation changes and growth. This figure is an update of the figure by Aber et al. (1998) (after De Vries and Schulte-Uebbing (2018)). It illustrates the trade-off between the initial positive impact of nitrogen enrichment on tree growth and related carbon sequestration on the one hand and the negative impact on ecosystem services (e.g. water quality regulation by nitrogen retention) and on biodiversity on the other hand.

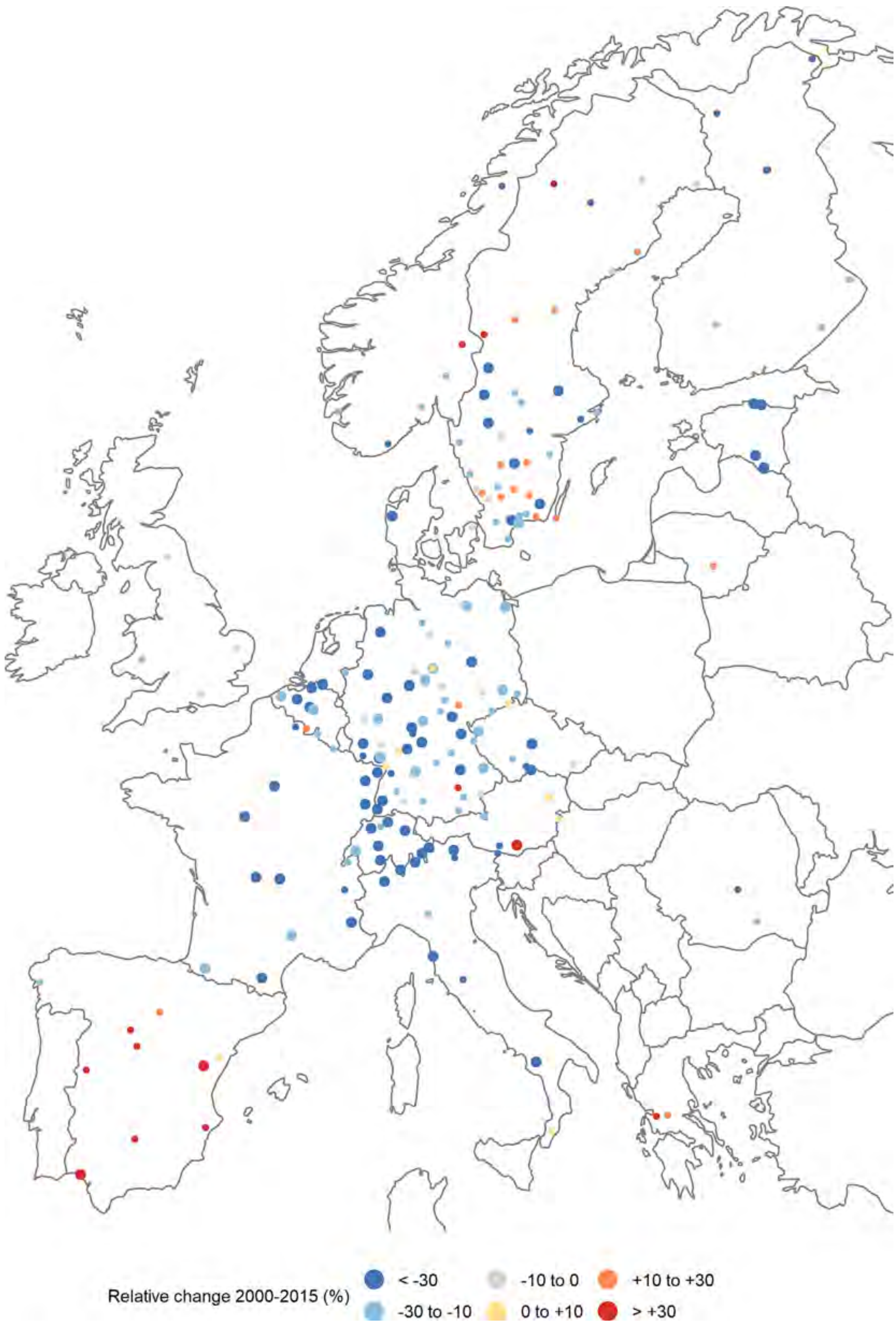

Fig. 2. Relative change of throughfall deposition of inorganic nitrogen at the intensive monitoring sites of the UNECE ICP Forests programme network between 2000 and 2015 (redrawn after Schmitz et al., 2018). Large dots indicate statistically significant trends; trends represented by small dots are not statistically significant.

of the environment that are directly relevant to people (e.g. tree growth) and *midpoint metrics*, i.e. parameters that are well-suited to measure progress towards desired environmental states (e.g. plant tissue concentrations) (Rowe et al., 2017). While results are limited to Europe, references have also been included relating to observations and experiments in the United States (US). For a detailed overview of impacts of decreased N deposition in the US, we refer to Gilliam et al. (2018, in press).

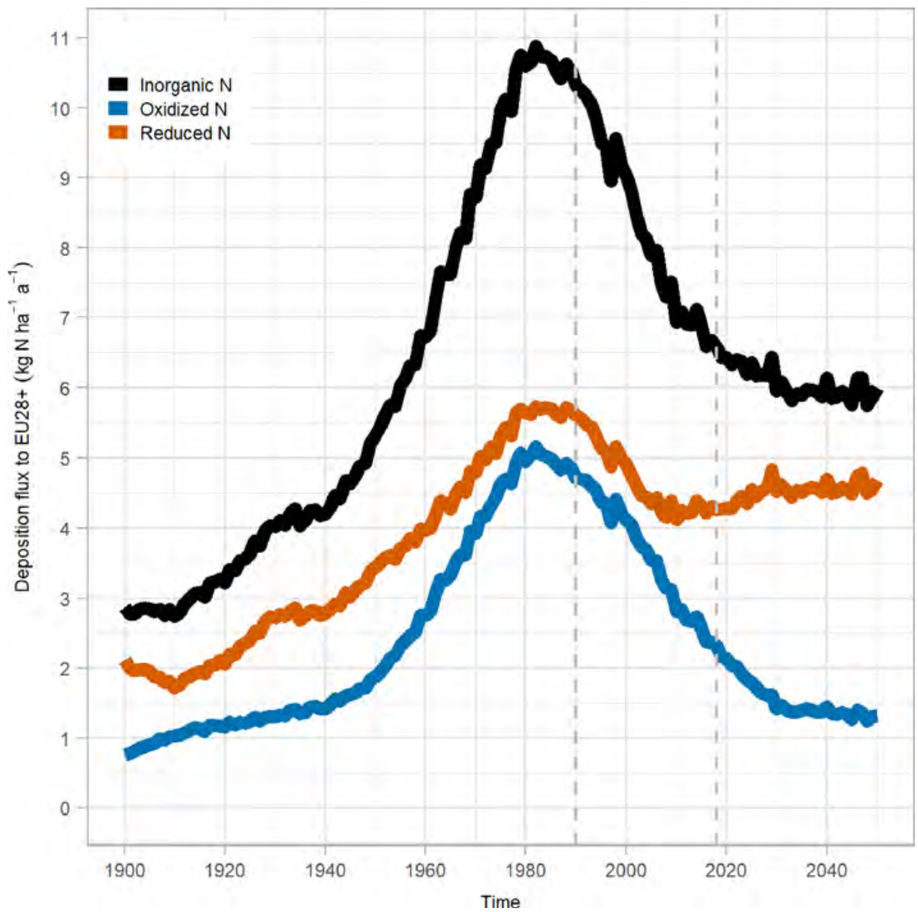

Fig. 3. Average deposition of oxidized, reduced and total N between 1900 and 2050 to the EU28, Norway and Switzerland according to EMEP model results (after Engardt et al. (2017), data kindly provided by Magnuz Engardt and David Simpson). Vertical dashed lines indicate the years 1990 and 2018. Future reductions are expected to be small and inorganic N deposition is likely converging to a level approximately twice as high compared to 1900.

2. Soil acidification and eutrophication

Atmospheric deposition of reactive nitrogen compounds such as nitrate (NO_3^-) and ammonium (NH_4^+) contributes to acidification and eutrophication of forest soils (Driscoll et al., 2006). Soil acidification involves accelerated losses of mineral nutrients (base cations, i.e. Ca^{2+}, K^+ and Mg^{2+}) and potential for the mobilization of toxic aluminium (Al), both of which can compromise tree health (Driscoll et al., 2006; Boudot et al., 1994; De Vries et al., 2014; De Wit et al., 2010). N deposition contributes to elevated soil solution NO_3^- concentrations and soil N stocks (Driscoll et al., 2001). This enrichment can have a variety of effects on trees and ground vegetation, covered in the subsequent chapters. NO_3^- concentrations in soil solution are a good indicator for the soil N status. Important determinants of NO_3^- leaching are the C/N ratio of the forest floor (Gundersen et al., 1998a) and N deposition rates (Dise and Wright, 1995), as well as a variety of other site and stand characteristics controlling the ecosystem N cycling (Lovett and Goodale, 2011). Generally, elevated NO_3^- concentrations in soil solution are an indication of N availability in excess of biotic demand. Spatial patterns of soil solution NO_3^- are highly variable but partly reflect spatial patterns in N deposition, with higher levels in the Netherlands, Belgium, parts of Germany, Switzerland, and Denmark and lower levels in parts of France, Norway, Northern Sweden, and Finland (Boxman et al., 2008; De Vries et al., 2007; Evans et al., 2001; Gundersen et al., 1998a; Jonard et al., 2012; Mellert et al., 2008; Moffat et al., 2002; Pannatier et al., 2010; Pihl Karlsson et al., 2011; Rothe et al., 2002; Ukonmaanaho et al., 2014; van der Heijden et al., 2011; Verstraeten et al., 2012). There are relatively fewer reports of elevated NO_3^- in soil solution in Southern and Eastern Europe, and N deposition is mostly lower in these regions (Waldner et al., 2014).

Observational studies

At the European scale, studies examining trends in soil solution N show weak or non-significant trends. For example, Johnson et al. (2018) found a weakly significant ($p < 0.1$) reduction in NO_3^- concentrations at 40–80 cm depth corresponding to a decrease of 30% over 10 years when analysing data from 162 plots across Europe between 1995 and 2012. They found no significant trend in 10–20 cm depth. An earlier analysis (from the early 1990s to 2006) using a similar dataset found mostly non-significant trends in soil solution inorganic N concentrations (Iost et al., 2012). These studies did not focus specifically on areas with high N deposition and included many sites from N limited areas of Northern Europe. Within Europe, national and regional studies show variable results. For example, in the Netherlands and Flanders soil solution NO_3^- declined in response to decreasing N deposition (Boxman et al., 2008; Verstraeten et al., 2012). In contrast, an intensive study at the site Solling in Germany found NO_3^- continued leaching from a spruce (*Picea abies*) stand and increased at a beech (*Fagus sylvatica*) stand despite decreasing N deposition between 1973 and 2013, indicating a reduction of the N retention capacity of the soil over

Table 1
Summary of trends in soil solution chemical characteristics indicative for eutrophication and acidification status (concentration of NO_3^-, base cations (BC, i.e. Ca^{2+}, K^+ and Mg^{2+}) and total aluminium (Al_{tot}), pH, equivalent ratio of BC and Al_{tot} (BC:Al_{tot}), acid-neutralizing capacity (ANC) and ionic strength) from studies across Europe.

Effect	Trend				
	↑	↑/↔	↔	↔/↓	↓
NO_3^-		Meesenburg et al. (2016) (Germany)	Johnson et al. (2013) (Ireland), Löfgren and Zetterberg (2011), Pihl Karlsson et al. (2011) (Sweden), Vanguelova et al. (2010) (UK)	Pannatier et al. (2010) (Switzerland), Sawicka et al. (2016) (UK), Ukonmaanaho et al. (2014) (Finland)	Boxman et al. (2008) (Netherlands), Oulehle et al. (2011) (Czech Republic), Verstraeten et al. (2012), Verstraeten et al. (2017) (Flanders)
pH	Akselsson et al. (2013), Löfgren et al. (2011) (Sweden), Verstraeten et al. (2016) (Flanders)	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)
BC			Vanguelova et al. (2010) (UK), Johnson et al. (2013) (Ireland)	Graf Pannatier et al. (2011) (Switzerland), Sawicka et al. (2016) (UK)	Jonard et al. (2012) (Wallonia), Verstraeten et al. (2012) (Flanders), Boxman et al. (2008) (Netherlands), Fölster et al. (2003), Akselsson et al. (2013) (Sweden)
Al_{tot}	Jonard et al. (2012) (Wallonia), Fölster et al. (2003) (Sweden)		Sawicka et al. (2016) (UK)	Vanguelova et al. (2010), Löfgren et al. (2011), Löfgren and Zetterberg (2011), Pihl Karlsson et al. (2011) (Sweden), Johnson et al. (2013) (Ireland)	Verstraeten et al. (2012) (Flanders), Boxman et al. (2008) (Netherlands)
BC:Al_{tot}		Meesenburg et al. (2016) (Germany)		Graf Pannatier et al. (2011) (Switzerland)	Verstraeten et al. (2012) (Flanders)
ANC	Akselsson et al. (2013), Löfgren et al. (2011) (Sweden), Verstraeten et al. (2012) (Flanders)	Fölster et al. (2003), Löfgren and Zetterberg (2011), Pihl Karlsson et al. (2011) (Sweden)			
Ionic strength				Löfgren and Zetterberg (2011) (Sweden)	Löfgren et al. (2011) (Sweden), Verstraeten et al. (2012) (Flanders), Vanguelova et al. (2010) (UK)

time (Meesenburg et al., 2016). Other studies found no trends in NO_3^- soil solution concentrations during periods of stable N deposition (e.g. Alewell et al., 2000.; Johnson et al., 2013; Pannatier et al., 2010). At a heavily acidified forest in the Czech Republic, NO_3^- concentrations in soil solution declined despite no decrease in N deposition. This was due to an increase in N uptake by vegetation and changes in organic matter cycling as the soil became less acidic (Oulehle et al., 2011).Where soil solution NO_3^- decreased, it is generally accompanied by a decrease in base cations and total Al concentrations, while soil solution pH and acid neutralizing capacity (ANC) showed no uniform trends in recent decades (Iost et al., 2012; Johnson et al., 2018). Recovery from acidification primarily occurs on poorly buffered, acidic soils while acidification progresses on better buffered soils despite large decreases in sulphur (S), and to a lesser degree, N deposition (Johnson et al., 2018). The absence of a uniform recovery of soil solution from acidification agrees with trends in bulk soil chemistry. Cools and De Vos (2011) found that base saturation increased in soils with low buffering capacity but decreased in soils with initially higher base saturation across Europe. A similar result was found for the Netherlands between 1990 and 2015 (De Vries et al., 2017a). Table 1 summarizes results on trends of soil solution eutrophication and acidification status from studies across Europe.

Experimental studies

In addition to observational studies, also field experiments provide information on changes of the soil chemical status under decreasing N deposition. In this context, the NITREX and EXMAN nitrogen manipulation experiments at several sites in Europe are a valuable source of information (Wright and Rasmussen, 1998). At three NITREX sites, throughfall N deposition was decreased from 36 to 50 kg N ha^{-1} a^{-1} to 5–16 kg N ha^{-1} a^{-1} by roofing. A decline in N leaching became apparent within the first three years of treatment at all three sites (Beier et al., 1998; Boxman et al., 1998; Emmett et al., 1998; Gundersen et al., 1998b). A similarly fast response in N leaching has been observed from a roofing experiment in southern Norway (Wright et al., 1993). These results indicate that continuous high N inputs are required to sustain N leaching in most forest ecosystems, suggesting that decreasing deposition quickly translates into improvements in soil water quality (Emmett et al., 1998). This, however, also implies that considerable amounts of N deposited over the last decades are retained and that the return of the ecosystem to the original N status is potentially slow (Gundersen et al., 1998b). In contrast to these findings, also unchanged or increased N leaching despite decreased deposition was occasionally reported from observational (Meesenburg et al., 2016) and experimental studies (Emmett et al., 1998).

Summary

Long-term monitoring data provides information on NO_3^- concentrations in soil solution as an indicator for the soil N status. Despite considerable heterogeneity, indications for a decreasing trend in soil solution NO_3^- concentrations at the European scale exist. Experimental studies tend to report a faster and more pronounced reaction of soil solution NO_3^- concentrations compared to the findings from large-scale observational studies. In the experiments the magnitude and speed of decrease in N supply was larger compared to trends in N deposition in most parts of Europe. Furthermore, longer-term changes in soil microbial activity (e.g. mineralization rates) might be reflected to a larger degree in the observational studies compared to experimental studies which often focus on the time period immediately after the onset of the artificial decrease of N supply. Nevertheless, both types of studies suggest indications of a response in soil solution NO_3^- concentrations to decreases in N deposition. Soil acidification shows non-uniform tendencies across Europe despite large-scale decreases in N, and especially S, deposition.

3. Understory vegetation

Forests provide habitat for understory vegetation, bryophytes, lichens as well as microbial and animal communities. While N is a limiting resource for many organisms (Vitousek and Howarth, 1991), the efficiency with which it is used is species-specific (Chapin, 1980). As a consequence, more N causes some species to thrive on the expense of others, usually causing a net loss in species diversity (Suding et al., 2005). Besides this effect on interspecific competition, changes in N deposition can also modify herbivory, interactions with fungi, and invasibility by exotic species, thereby affecting understory species composition (Gilliam, 2006). In managed forests these mechanisms are rarely reflected in the composition of the main tree species for they are typically intentionally chosen by forest managers. In contrast, forest understory vegetation, bryophytes, lichens, mycorrhiza, and soil fauna can be expected to be affected by N availability in addition to other environmental factors such as light availability, temperature, moisture, and nutrients other than N. The responses of these groups to elevated N deposition encompass changes in the abundance of species, alteration in the identity of species (species composition), and pauperization of local and regional species diversity (Bobbink et al., 2010; Farrer and Suding, 2016; Hautier et al., 2009; Nijssen et al., 2017). Fig. 4 exemplifies effects of N deposition on forest understory vegetation for lichen diversity and herb layer plant community composition.

Observational studies

While there are several observational studies on the reaction of forest understory diversity to elevated N deposition, to our knowledge, none of them focused specifically on the response to declining N deposition. These studies confirm an increase in nitrophilic forest understory plant species on the expense of oligophilic species both in European-wide (Dirnböck et al., 2014; van Dobben and De Vries, 2017) as well as regional contexts (Bobbink and Hettelingh, 2011 and references therein; Heinrichs and Schmidt, 2016; Keith et al., 2009; Roth et al., 2015). Besides N deposition, litter quality, light availability, density of large herbivores, and differences in forest management were also important drivers of change in understory plant communities (Bernhardt-Römermann et al., 2015; Perring et al., 2017; Verheyen et al., 2012). These changes in species composition do not, however, seem to be accompanied by a broad scale, synchronized decline in plant diversity in European forests (Dirnböck et al., 2014; van Dobben and De Vries, 2017; Verheyen et al., 2012).

In contrast, elevated N deposition has clearly contributed to a dramatic diversity loss in epiphytic lichens in many European forests (Bobbink and Hettelingh, 2011; Giordani et al., 2014; Hauck et al., 2013; Mayer et al., 2013). Similarly, major impacts in the

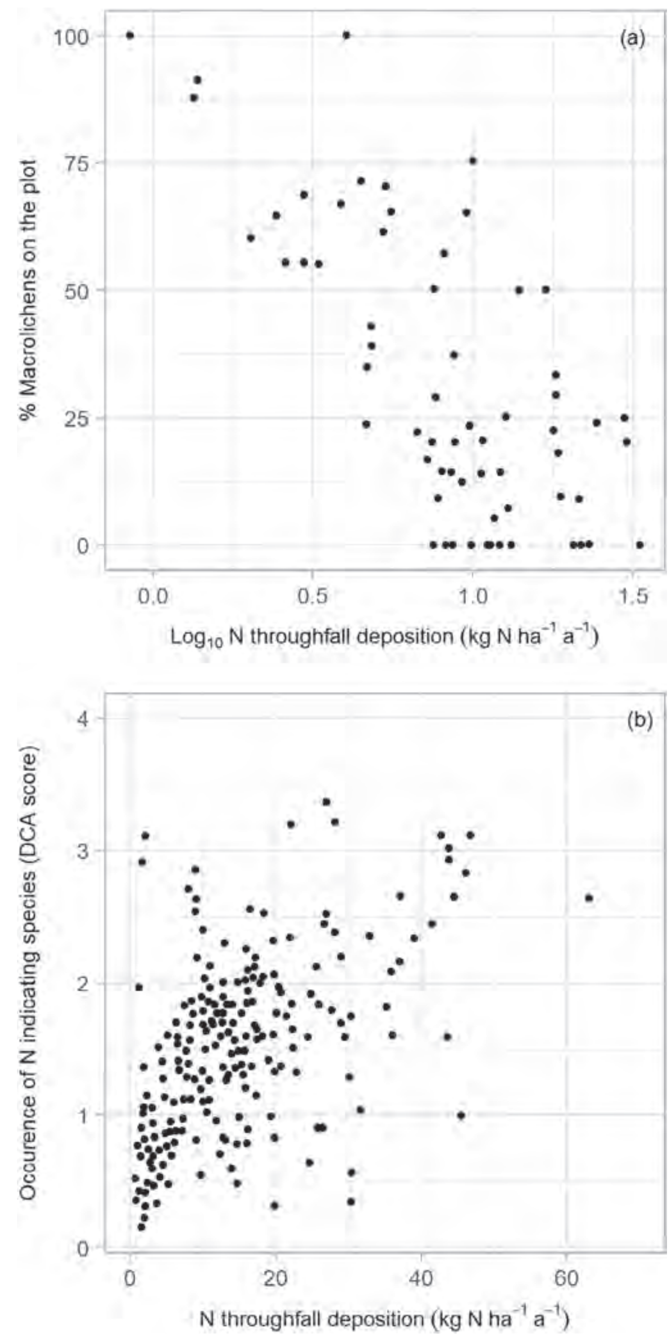

Fig. 4. Examples for the effects of N deposition on forest understory vegetation. (a) Relationship between lichen diversity (proportion of macrolichen species among all lichen species) and N throughfall deposition based on 83 forest plots across Europe. Reprinted from Giordani et al. (2014) with permission from Elsevier. (b) Relationship between the occurrence of nitrogen indicating species and N throughfall deposition based on a detrended correspondence analysis (DCA) of the floristic composition of the herb layer at 488 forest plots in the nemoral zone of Europe. Scores on the fourth axis of the DCA are positively correlated with nitrogen deposition. Redrawn from Seidling et al. (2008) by permission of the publisher (Taylor & Francis Ltd, http://www.tandfonline.com).

community composition and diversity of mycorrhiza were identified at the European level (Suz et al., 2014; van der Linde et al., 2018) and in various regional studies (Bobbink and Hettelingh, 2011, references therein). Furthermore, diversity effects of N deposition on one receptor can indirectly affect others such as soil fauna and mammals because effects cascade from e.g. plants to animal species (Nijssen et al., 2017) or from soil microbes to plants (Farrer and Suding, 2016). However, studies detailing the link between N deposition and animal diversity in Europe's forests are scarce, partly due to the complex dynamics of animal populations and corresponding food-webs (Nijssen et al., 2017).

Experimental studies

In addition to these findings from observational studies, a limited number of N manipulation experiments report on changes in understory vegetation in response to decreasing N input. Strengbom et al. (2001) compared vascular plant, fungi, and bryophyte communities between control and treatment plots at two experimental forest sites in Sweden where N fertilization was cancelled nine and 47 years prior to the analyses, respectively. They found differences in the vascular plant community at the site where treatment ended nine years ago but no longer at the site where treatment was cancelled 47 years ago. Nevertheless, the fungi and bryophyte communities deviated from the control plots at both sites. Sujetovienė and Stakėnas (2007) report on changes in pine forest understory plant community in response to drastic emission reductions from a close-by fertilizer plant in Lithuania. They found a decrease in nitrophilous species within the 16 years between two ground vegetation studies (1988 and 2004). It should be noted that also the light conditions and the acidity status of the respective forest stands changed over the same time. In one of the NITREX experiments, N-indicating fern cover significantly decreased after 5 years of reduction of N deposition from 60 kg N ha^{-1} a^{-1} to 5 kg N ha^{-1} a^{-1} by roofing. A recovery of other species was not recorded (Boxman et al., 1998).

Also findings from grassland vegetation experiments might be informative for the question of forest understory vegetation response to decreasing N deposition. Stevens et al. (2012) found significant differences in Ellenberg N values between control and treatment plots 15 years after cessation of N fertilization in mesotrophic grassland in the UK. Shi et al. (2014) report on the vegetation composition three years after cessation of N fertilization at a sandy grassland site in Northeast China. They found that the vegetation at the control and the formerly treated plots still differed although indications for an ongoing process of recovery were apparent. Storkey et al. (2015) report that grassland biodiversity largely recovered over a period of 20 years of decreasing ambient N deposition, based on observations from the control plot of a fertilization experiment in the UK. The pronounced recovery was potentially supported by the regular export of N from the ecosystem by haying (Tilman and Isbell, 2015).

Summary

Recent studies based on large-scale monitoring data find shifts in understory community composition in response to high levels of N deposition but do not report on responses to decreasing N deposition. Results from experimental studies suggest that while the recovery of understory vegetation from high N inputs is possible, time-lags in the order of decades are to be expected. One mechanism causing these delays is that in regions where high N deposition eradicated source populations, back-colonization will be particularly difficult (Clark and Tilman, 2010; Dullinger et al., 2015). The complex consequences of such effects have already been shown for land management legacies' impact on dispersal dynamics and subsequent community alterations (e.g. Burton et al., 2011). Strong recovery delay due to dispersal limitation can be expected for epiphytic lichens because regional species extinctions were particularly pronounced (Hauck et al., 2013). We hypothesize that this delay in the response of understory vegetation to decreases in N deposition partly explains the absence of corresponding trends in Europe-scale observational studies. In addition, changes in other environmental conditions like light availability, forest management, sulphur deposition, habitat loss and fragmentation, climate impact, and non-native species invasion (see e.g. Perring et al., 2017) superimpose on the signal of N deposition in forest understory communities.

4. Tree nutrition

Foliar element concentrations and their ratios reflect the nutritional status of trees. Unbalanced N:P ratios in foliar tissues are frequently associated with defoliation (Bontemps et al., 2011; Ferretti et al., 2015; Veresoglou et al., 2014; Waldner et al., 2015) and an increasing risk of attacks by parasites (Flückiger and Braun, 1998) and herbivores (Pöyry et al., 2016) as well as decreasing plant capacity to respond to abiotic stressors such as drought, warming, and frost (Fangmeier et al., 1994; Sardans and Peñuelas, 2012). Furthermore, changes in N:P ratio in foliar tissues can have several consequences in forest trophic chains (Peñuelas et al., 2013). For example, increases in foliar-litter N:P ratios have been associated with shifts in community composition and decreases in species richness in soil communities and understory vegetation in some European forests (Peñuelas et al., 2013). Unbalanced plant N:P ratios can reduce the resistance to biotic stressors such as the competition against invasive species (Sardans et al., 2016a).

Observational studies

The status and trends of tree nutrition are highly variable across Europe. At the European scale, two recent studies report tendencies of decreasing foliar N concentrations for beech and oak, covering the periods 1992–2009 and 2000–2015, respectively (Jonard et al., 2015; Sanders et al., 2017b). To a lesser extent, decreases are also indicated for spruce, while stable or slight increasing foliar N concentrations are reported for pine (*Pinus sylvestris*). At the same time, however, the mass per needle/leaf significantly increased for spruce and beech, causing an overall increase in the N content per needle/leaf despite the decreasing concentrations ("dilution effect", Jonard et al., 2015). At the local or regional level, studies based on data from 1990 onward report stable N concentrations or moderate changes in both directions (Jonard et al., 2012; Verstraeten et al., 2017; Wellbrock et al., 2016). Analysis restricted to, or including data from before 1990 frequently (Duquesnay et al., 2000; Hippeli and Branse, 1992; Mellert et al., 2004 for pine; Prietzel et al., 1997; Sauter, 1991) but not always (Braun et al., 2010; Mellert et al., 2004) report increasing foliar N concentrations or contents across Europe. Although not focused on temporal trends, other studies suggest a general effect of N deposition on foliar N concentrations based on analyses of large-scale spatial data (De Vries et al., 2003; Sardans et al., 2016b).

Foliar P concentrations decreased continuously according to studies analyzing data from 1990 onward in the important forest species in central and northern Europe, such as pine, spruce, beech, and sessile oak (*Quercus petraea*), resulting in low or deficient foliar P status on 22%–74% of the plots depending on tree species (Ferretti et al., 2015; Jonard et al., 2015, 2012; Talkner et al., 2015). For N:P, increasing ratios have been observed in several studies at European scale based on data after 1990 (Jonard et al., 2015; Sanders et al., 2017a; Talkner et al., 2015). Apart from N:P imbalances, also trends towards increasing N:K and N:S ratios have been observed in a Europe-wide study while the N:Mg ratio was decreasing (Jonard et al., 2015). N deposition can cause deficiencies in other nutrients than N and nutrient imbalances due to a range of effects, including stimulation of plant growth (dilution effect) and negative effects on tree nutrient acquisition by modifying mycorrhizal associations (De Witte et al., 2017; Jonard et al., 2015; Peñuelas et al., 2013; Sardans et al., 2016b). Thus, the decreasing tendencies in foliar concentrations of nutrients other than N and increasing N:other element ratios suggest that N availability is still high in many regions across Europe and do not imply a recovery from high N deposition yet.

Experimental studies

Besides observational studies, a number of experiments provide indication on the reaction of foliar element concentrations to decreased N supply. In one of the abovementioned NITREX roofing experiments, a decrease in needle N concentrations and an improvement (reduction) of the N:Mg and N:K ratio is documented after three years (Boxman et al., 1998). At the other two sites, no significant reductions in foliar N concentrations were observed six years after the treatment started (Emmett et al., 1998). Högberg et al. (2006) report average foliar element concentrations for the time period seven to twelve years after the cessation of an N addition treatment. Foliar N concentration clearly decreased and other elements showed minor increases. Twenty years after termination of the N fertilization at the same site, foliar N concentrations were still slightly elevated compared to the control (Högberg et al., 2014). Similarly, Blaško et al. (2013) report a recovery (decrease) of foliar N concentrations based on measurements 17 and 19 years after the termination of a N fertilization experiment, while also still slightly exceeding the levels at the control plot. Results from grassland and moorland fertilization experiments report that foliar N concentrations had decreased when measured 7–15 years after cessation of the N addition (Clark et al., 2009; Edmondson et al., 2013; Stevens et al., 2012). These findings from experiments indicate that decreases in N deposition can be expected to be reflected in foliar N concentrations with a lag time of a several years.

Summary

Despite the large heterogeneity in trends in tree nutrition, studies based on large-scale long-term monitoring data report tendencies of decreasing foliar N concentrations for beech, oak and to a lesser extent for spruce. The degree to which the decreasing trends in N deposition contribute to these trends is not clear. On the one hand, decreasing tendencies of NO_3^- concentration in soil solution (see "Soil acidification and eutrophication"), findings from experimental studies as well as large-scale studies documenting the relation between spatial patterns of N deposition and foliar N concentrations suggest that the decrease in N deposition could have affected foliar N concentrations. On the other hand, the cutback in N deposition across Europe is typically far smaller compared to experimental treatments and might not yet have led to a widespread decrease in N availability for tree nutrition in a relevant magnitude (Braun et al., 2010; Mellert et al., 2017; Riek et al., 2016). The increase in foliar mass (dilution effect, Jonard et al., 2015) likely explains a considerable proportion of the decrease in foliar N concentrations. Furthermore, decreasing tendencies in other elements and increasing N:other element ratios do not indicate recovery from high N availability. Further analyses are required to gain a better understanding where and to what extent changes in N deposition or other mechanisms control tree nutrition across Europe and which time lags are involved.

5. Tree vitality

The concept of "vitality" of forests is linked to several interrelated aspects, including above- and below-ground growth, tree nutrition as well as the susceptibility of trees to biotic (e.g. insects) and abiotic (e.g. climatic extremes) stress. Tree crown condition is often interpreted as an aggregated measure of tree vitality because it reflects the impacts of several different environmental drivers. It is typically measured in the form of the degree of `crown defoliation' (Eichhorn et al., 2016).

Observational studies

Several studies addressed the link between nitrogen deposition and defoliation at the European scale (e.g. Ferretti et al., 2015; Klap et al., 2000) but to our knowledge none reports explicitly on the effect of decreased N deposition. Existing studies focus on the relative importance of air pollution among other determinants of crown condition like climate, soil, and stand age. The results reflect the complexity and spatial heterogeneity of the underlying processes. For example, Ferretti et al. (2015) found that N-related variables improved defoliation models based on data from 71 plots across Europe. Higher N deposition led to higher percentage of defoliated trees for beech and spruce, while the effect was opposite for pine. Similarly, Vitale et al. (2014) and De Marco et al. (2014) found aspects of N deposition to be relevant determinants of crown condition for several species across Europe, with varying direction of the effect. Other studies found weak or no relation between defoliation and N deposition (Hendriks et al., 2000; Klap et al., 2000; Solberg and Tørseth, 1997; Staszewski et al., 2012). In a regional study, Armolaitis and Stakenas (2001) report on the response of the crown condition of a pine forest to emission reductions from a close-by fertilizer plant in Lithuania. Refoliation began 6–7 years after the decrease of air pollution.

N-induced effects on vitality

The mechanisms by which excess N supply can cause a net decrease in tree vitality can be complex, interlinked and only episodically apparent, including increased susceptibility to insect attacks, pathogens, frost and storm damages (Bobbink and Hettelingh, 2011), changes in mycorrhiza (Arnolds, 1991; Braun et al., 2010; De Witte et al., 2017; Duquesnay et al., 2000; Jaenike, 1991; van der Linde et al., 2018), changes in the rooting system and aluminum toxicity to roots (Dziedek et al., 2017; Godbold and Kettner, 1991; Haynes, 1982; Jonard et al., 2012; Ostonen et al., 2007), depletion of base cations due to NO_3^- leaching (Jonard et al., 2012; Prietzel et al., 1997) or problematic P supply (Jonard et al., 2015; Mellert and Ewald, 2014; Neirynck et al., 1998; Ochoa-Hueso et al., 2013; Peñuelas et al., 2013; Sardans et al., 2015; Sardans and Peñuelas, 2012; Thelin et al., 1998). Tree species, stand age, soil, and meteorological conditions as well as other local factors co-determine these symptoms.

Summary

Tree crown condition provides an aggregated measure of tree vitality. Studies evaluating spatial and temporal patterns of crown condition based on long-term monitoring data come to different conclusions regarding the relative importance and direction of the effect of N deposition. To our knowledge, no large-scale response to decreasing N deposition has been reported. N deposition can have both a positive (fertilizing) effect on tree vitality (crown condition) but also contribute to a range of adverse effects. We assume that the high complexity and spatio-temporal variability of these mechanisms is partly causing the difficulty to detect signals of decreasing N deposition in tree vitality. In addition, factors like site, stand age, drought, and frost can have strong effects on vitality independent of N deposition (e.g. Eickenscheidt et al., 2016; Klap et al., 2000).

6. Tree growth

Tree growth provides the primary economic benefit from most forest sites and is an important process in forest CO_2 budgets. Aber et al. (1998) hypothesized that net primary production of trees will show an increasing followed by a decreasing (unimodal) response with ongoing nitrogen saturation (comp. Fig. 1). The underlying assumption is that low to moderate levels of N deposition will relieve trees from growth limitation due to originally widespread N shortage (Aber et al., 1995; De Vries et al., 2009; Kahle, 2008; Schulte-Uebbing and De Vries, 2017; Solberg et al., 2009; Sutton et al., 2008; Vitousek and Howarth, 1991). However, when N deposition exceeds a certain level, the stimulating effects diminish due to the antagonistic effects applying to overall tree vitality (see above), e.g. of soil acidification, nutrient imbalances and increased susceptibility to biotic and abiotic stress (Aber et al., 1998; De Vries et al., 2014; Dobbertin, 2005). For example, beneficial effects for tree growth by recovery from acidification have been documented in Europe and the US (Mathias and Thomas, 2018; Juknys et al., 2014).

Observational studies

There are various broad-scale and regional studies investigating the effect of N deposition on tree growth, while accounting for the impacts of other drivers, such as changes in temperature and precipitation (e.g. Braun et al., 2017; Kint et al., 2012; Kolář et al., 2015; Solberg et al., 2009). In these studies, changes in growth patterns have rarely been explicitly linked to declining trends in nitrogen deposition. In some cases, a simultaneous decrease in S and N deposition complicated the separation of effects (Juknys et al., 2014; Nellemann and Thomsen, 2001). However, the results of these studies provide indications for the threshold level of N deposition at which growth enhancement and growth reductions can be expected (Braun et al., 2017; Kint et al., 2012). For example, field monitoring data of forest growth at more than 300 plots in Europe suggest a non-linear growth response to N deposition between 3 and 60 kg N $ha^{-1}yr^{-1}$ with a threshold near 35 kg N $ha^{-1}yr^{-1}$ (Solberg et al., 2009). Kint et al. (2012) documented a non-linear growth response, in terms of basal area increment (BAI), to increasing N availability for 180 oak and beech plots in Flanders throughout the 20th century (the period 1901–2008). They found positive effects of N deposition on BAI up to 20–30 kg N ha^{-1} yr^{-1} and declining growth above these levels. Etzold et al. (2014) found a non-linear relation between NPP and N deposition, with the positive effect flattening off at sites with an N deposition above 20 kg N $ha^{-1}yr^{-1}$, based on data from intensive monitoring plots in Switzerland. In experimental and observational studies in forests in Switzerland, Flückiger et al. (2011) found a growth-stimulating effect of N which turned into no effect or a decrease of growth with increasing duration or magnitude of the N input. Anders et al. (2002, in Bobbink and Hettelingh, 2011) reported growth-reducing effects of N deposition on Scots pine stands in the north-east of the German Northern Lowland in the vicinity of N emission sources with deposition rates exceeding 35 kg N ha^{-1} a^{-1}, while for other locations and tree species, accelerated growth was observed at open field deposition rates exceeding 10–15 kg N ha^{-1} a^{-1}.

Experimental studies

Further information on the growth response of trees to different levels of N deposition originates from field experiments. For example, in one of the NITREX experiments, Boxman et al. (1998) report a significant increase in growth after three years of artificially decreasing N deposition rates by roofing. It should be noted, however, that in this experiment not only N but also S deposition decreased. Högberg et al. (2006) found that very high rates of N addition (90–180 kg N ha^{-1} a^{-1}) led to an increase in tree growth only until a cumulative amount of approximately 1 t N ha^{-1} while further N addition lowered the gain in wood volume. In a similar experimental setup, Blaško et al. (2013) observed that a strongly fertilized plot (90–180 kg N ha^{-1} a^{-1}) had a lower long-term average productivity than other fertilization levels (30–120 kg N ha^{-1} a^{-1}) but still more than the control plot. These results support the perspective that improved N supply has a positive effect on growth in case of N limitation and can act negatively in case of excess N (Flückiger et al., 2011).

Global meta-analyses also confirm thresholds in the growth response of trees to N deposition. For example, Tian et al. (2016) analysed a dataset of 44 experimental studies from wetland, grassland, temperate, and boreal forest (most data are from temperate forest). They found that the effect of N input on aboveground net primary production switches from increase to decrease at approximately 50–60 kg N ha^{-1} a^{-1}. Schulte-Uebbing and de Vries (2017) found that the N-induced increase in carbon sequestration was significantly lower at higher ambient N deposition rates (above 15 kg N ha^{-1} a^{-1}), reviewing results from forest fertilization experiments in temperate, boreal, and tropical forests. Field data of maximum rates of photosynthesis against N deposition for 80 forested plots over the world indicated an increase in photosynthesis up to an N deposition near 10–15 kg N ha^{-1} a^{-1} followed by no further change up to 35 kg N ha^{-1} a^{-1} (Fleischer et al., 2013).

Summary

We did not find an indication for a large-scale response in tree growth to decreasing N deposition. However, results from observational and experimental studies corroborate the concept of a unimodal response of tree growth to N deposition. Estimates of thresholds above which N deposition negatively affects tree growth range from as low as 15–20 kg N ha^{-1} a^{-1} to very high levels only relevant under experimental conditions. This suggests that particularly polluted forest stands (mostly located in Central and Western Europe) might have benefitted from declining N deposition, as decreases have been strongest in the formerly most polluted regions. Few trends of decreasing N deposition have been observed in less polluted areas like Northern Scandinavia, suggesting that a growth decline due to decreased N deposition in these areas is less likely.

7. Conclusion and outlook

Results from observational studies across Europe for responses in soil, ground vegetation, and trees (nutrition, growth and vitality) to decreasing N deposition indicate considerable spatial variability in the trends published for these parameters. For soil solution NO_3^- concentrations and potentially also for changes in foliar N concentrations, indications for a reaction to decreased nitrogen deposition exist. We found several studies reporting on the effects of N deposition on understory vegetation, tree growth or tree vitality, but none of them focused specifically on responses to declining N deposition. For tree growth, these studies suggest a positive effect at low to moderate levels of N deposition and no or adverse effects at high levels. In line with these findings from observational studies, experimental studies also report more pronounced reactions of soil solution and foliar concentrations to decreased nitrogen deposition compared to the other parameters. Stevens (2016) reviewed experimental and observational studies in grasslands, heathlands, wetlands, and forests for information on the speed of recovery from high N deposition. Mainly in line with our findings, they report a relatively rapid response for mobile or plant-available forms of N in soil chemistry and for N contents in plant tissues across habitats (with the exception of forests showing a slower response in foliar element concentrations compared to other habitats). Similarly, Rowe et al. (2017) suggest N leaching rates and (moss) tissue N concentrations as midpoint-metrics, i.e. as indicators for effects-based monitoring of progress towards pollution reduction targets, due to their dynamic response to changing N deposition rates.

Linking results from observational and experimental studies is problematic due to the more controlled conditions and the typically faster and stronger cutback of N supply rates in experimental settings compared to real-world decreases in N deposition. A multitude of confounding factors, including the joint decrease of N and S deposition (e.g. Armolaitis and Stakenas, 2001) complicate the interpretation of results from observational studies. Furthermore, many of the large-scale observational studies reviewed in this paper are based on plots which are not distributed representatively across Europe. The larger monitoring efforts in Central and Western Europe likely led to an overrepresentation of plots where N deposition remained on a high level despite comparatively large decreases of N deposition.

Future decrease of N deposition to forests in Europe and associated ecosystem responses will most likely be limited (Fig. 3). Simpson et al. (2014) expect only minor reductions in the European ecosystem area with exceedances of the critical load for nutrient nitrogen (from 64% in 2005 to 50% in 2050). Under the assumption that soil solution NO_3^- concentrations and potentially also foliar N concentrations track changes in N inputs with a delay of only a few years (see above), limited changes of these parameters in response to declining N deposition would be expected for the future. For tree vitality and vitality-related growth effects, time-lags in the recovery from excess N deposition might be expected due to slow reversal of N-induced soil acidification and changes in mycorrhizal association. For understory vegetation community composition it has to be questioned whether full recovery can be expected at all since forest biodiversity is facing a number of additional “extinction debts” such as habitat loss and fragmentation, climate impact, and non-native species invasion (see e.g. Perring et al., 2017) likely causing further decline in biodiversity (Essl et al., 2015). If at all, these recovery processes will, however, only become apparent in regions with sufficient absolute magnitude of the cutback in N deposition. Furthermore, responses will likely be highly heterogeneous in space controlled by site-specific conditions.

In view of our results, a simple reversal of the stages of the classical nitrogen saturation concept (Fig. 1) does not seem to reflect the observed and expected responses to decreasing N deposition appropriately. Instead, several forest ecosystem properties seem to react with varying degrees of delay to cutbacks in N deposition. Correspondingly, the overall forest ecosystem state develops on a different trajectory during the process of N de-saturation compared to N saturation. This hysteresis behavior is in line with findings from Gilliam et al. (2018, in press), who review results for soil acidification, plant biodiversity, soil microbial communities, forest carbon (C) and N cycling, and surface water chemistry focusing on the US. In view of the high variability of forest ecosystems, a set of “recovery types” could potentially serve to roughly classify the development of major strata of forest sites under decreasing N deposition. For analytic and predictive purposes, more detailed models will be required to adequately represent processes of N (de-)saturation. In particular, dynamic modelling approaches taking complex microbial soil N processes into account may provide insights into the developments of forest ecosystem N pools accumulated over the last decades (Akselsson et al., 2016; Bonten et al., 2016; Dirnböck et al., 2017; Fleck et al., 2017; Rizzetto et al., 2016; Yu et al., 2016). Under the expected limited future decrease in N deposition, other controlling factors like climate change and forest management strategies will probably dominate the changes in N-enriched forests.

Funding sources

Thomas Dirnböck was funded by the project ACRP7 - WOOD-N-CLIMATE, Austria [grant number KR14AC7K11858]. Josep Peñuelas and Jordi Sardans would like to acknowledge the financial support from the European Research Council Synergy grant ERC-SyG-2013-610028 IMBALANCE-P.

Declarations of interest

None.

Acknowledgements

Thanks to Magnuz Engardt and David Simpson for providing the time series on reduced and oxidized N deposition to Europe according to the EMEP model as published in Engardt et al. (2017).

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3. Comparison of Methods for the Estimation of Total Inorganic Nitrogen Deposition to Forests in Germany

Ahrends, B.; Schmitz, A.; Prescher, A.-K.; Wehberg, J.; Geupel, M.; Andreae, H.; Meesenburg, H.

Published Journal Article, Frontiers in Forests and Global Change 2020, 3.

https://doi.org/10.3389/ffgc.2020.00103

frontiers in Forests and Global Change

ORIGINAL RESEARCH
published: 16 September 2020
doi: 10.3389/ffgc.2020.00103

Comparison of Methods for the Estimation of Total Inorganic Nitrogen Deposition to Forests in Germany

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OPEN ACCESS

Edited by:
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Specialty section:
This article was submitted to Forests and the Atmosphere, a section of the journal Frontiers in Forests and Global Change

Received: *24 June 2020*
Accepted: *07 August 2020*
Published: *16 September 2020*

Citation:
Ahrends B, Schmitz A, Prescher A-K, Wehberg J, Geupel M, Andreae H and Meesenburg H (2020) Comparison of Methods for the Estimation of Total Inorganic Nitrogen Deposition to Forests in Germany. Front. For. Glob. Change 3:103. doi: 10.3389/ffgc.2020.00103

A reliable quantification of total inorganic nitrogen (TIN) deposition to forests is required for the evaluation of ecological effects of TIN inputs to forests and to monitor the success of clean-air policy. As direct measurements are scarce, different modeling approaches have been developed to estimate TIN deposition to forests. Three common methods are the (i) "canopy budget model," (ii) "inferential method," and (iii) "emission based estimates" using a chemical transport model. Previous studies have reported considerable and site-specific differences between these methods, complicating the interpretation of results. We use data from more than 100 German intensive forest monitoring sites over a period of 16 years for a cross-comparison of these approaches. Non-linear mixed-effect models were applied to evaluate how factors like meteorology, terrain and stand characteristics affect discrepancies between the model approaches. Taking into account the uncertainties in deposition estimates, there is a good agreement between the canopy budget and the inferential method when using semi-empirical correction factors for deposition velocity. Wet deposition estimates of the emission based approach were in good agreement with wet-only corrected bulk open field deposition measurements used by the other two approaches. High precipitation amounts partly explained remaining differences in wet deposition. Larger discrepancies were observed when dry deposition estimates are compared between the emissions based approach and the other two approaches, which appear to be related to a combination of meteorological conditions and tree species effects.

Keywords: nitrogen, canopy budget model, inferential method, forest, deposition, Germany

INTRODUCTION

During the last 70 years emissions of nitrogen (N) species to the atmosphere from traffic, industrial processes, and agriculture have drastically increased over pre-industrial levels and a significant decrease in the next decades in Europe is not expected (Simpson et al., 2014). The resulting atmospheric deposition of inorganic N to forests is an important determinant of tree growth

(Etzold et al., 2020), rendering nitrogen deposition an essential input variable in decision support systems for forestry under environmental change (Panferov et al., 2011; Thiele et al., 2017) and carbon uptake (Du and De Vries, 2018). Accurate quantification of N deposition is also necessary for the estimation of nitrate leaching from forest ecosystems (MacDonald et al., 2002; Johnson et al., 2018; Vuorenmaa et al., 2018) and the calculation of N budget changes in forest soils (Fleck et al., 2019). On a political and administrative level, N deposition estimates are required to assess the success of clean air policy (Hettelingh et al., 2017), the exceedance of critical loads for eutrophication and acidification (De Vries et al., 2015) and in the context of licensing procedures for nitrogen emitting facilities.

The total deposition (TD) of N into forest ecosystems occurs via three pathways (Unsworth and Fowler, 1987): Wet deposition (WD) comprises deposition via rain, snow and hail; dry deposition (DD) consists of gases and particles deposited on surfaces or directly taken up by vegetation; and occult deposition (OD) refers to the deposition of fog. DD and OD to forests is typically larger compared to other land cover types, due to the large surface area of the canopy and their high aerodynamic roughness. The sum of DD and OD is also referred to as interception deposition (ID, Ulrich, 1994). Unlike WD, which is fairly easy to assess (Staelens et al., 2008; Dämmgen et al., 2013), the quantification of ID is much more challenging. As OD is often of orographic origin, it usually only contributes significantly to TD in mountainous regions (Kirchner et al., 2014; Hunová et al., 2016).

The accurate quantification of DD fluxes to forests is still challenging due to a large variety of N species, their chemical reactivity, a high uncertainty in the estimation of deposition velocities (Saylor et al., 2019) and different deposition pathways including bi-directional fluxes (Wichink Kruit et al., 2012). Currently, micrometeorological methods (e.g., eddy covariance and gradient techniques) are regarded as the most accurate approaches to quantify DD and OD (Marques et al., 2001; Mohr et al., 2005; Schmitt et al., 2005; Brümmer et al., 2020). However, micrometeorological methods require a considerable measurement effort and observational data are therefore typically only available for short observation periods at a limited number of locations.

Three other methods are frequently used where information on deposition of total inorganic nitrogen (TIN) is required. Firstly, the canopy budget model (CBM) approach developed by Ulrich (1994) and modified many times (e.g., Draaijers and Erisman, 1995; De Vries et al., 2001; Staelens et al., 2008) is applicable where assessments of open field and throughfall precipitation and element concentrations are available, e.g., for intensive forest monitoring sites (De Vries et al., 2003; Meesenburg et al., 2004, 2016; Talkner et al., 2010). The application of the Ulrich (1994) CBM is straightforward and requires no empirical parameters. However, estimates of TIN deposition with CBM are questionable due to debatable assumptions, limited understanding of canopy ion exchange processes and propagation of measurement errors in calculations (Staelens et al., 2008; Adriaenssens et al., 2013).

Secondly, for monitoring sites with observations of ambient air concentrations of major gaseous N species (e.g., NH_3 and NO_2), DD can be estimated using the inferential method (IFM), i.e., by multiplying the concentrations with deposition velocities (Zimmermann et al., 2006). A variety of approaches is used to inform deposition velocities, ranging from dynamic models based on stomatal conductance and atmospheric conditions to land-use specific empirical long-term averaged deposition velocities (e.g., Schrader and Brümmer, 2014). At an intermediate level of complexity, published deposition velocities are adapted for site specific conditions based on semi-empirical correction factors (Schmitt et al., 2005; Kirchner et al., 2014). The IFM approach suffers from considerable variances in deposition velocities as shown by different review studies (e.g., Staelens et al., 2012; Schrader and Brümmer, 2014). In addition, the observation of NO_2 and NH_3 ambient air concentrations yield an extra uncertainty of ±30% (Schaub et al., 2016). At the end, DD calculated with the IFM needs to be combined with measurements of WD to yield TIN TD.

The third method to estimate TIN deposition is a combination of emission inventories and a chemical transport model using meteorological data for the simulation of the regional circulation (referred to as emission based method, EBM, in the following). A range of modeling systems exist (Vivanco et al., 2018). For Germany, the German Environmental Agency has funded the development of an emission-based approach that yields features with a higher spatial resolution compared to some European scale models (Schaap et al., 2018). Approaches with higher spatial resolution have been used in Germany for many years (Gauger et al., 2008; Builtjes et al., 2011; Schaap et al., 2015, 2017, 2018) and its results have been included in numerous impact studies (Hauck et al., 2012; Fleck et al., 2017, 2019; Thiele et al., 2017). In Germany, the EBM approach integrates emission inventories and a large number of local measurements of wet or bulk deposition to TIN deposition estimates with complete spatial coverage. Major challenges lie in the accuracy and spatio-temporal resolution of emission data and the parametrization of receptor-specific deposition processes with respect to DD and OD (Saylor et al., 2019).

Previous studies comparing TIN deposition derived with different methods occasionally reported considerable site-specific discrepancies. This is true for micrometeorological methods and CBM (Marques et al., 2001; Mohr et al., 2005), IFM and CBM (Schmitt et al., 2005; Kirchner et al., 2014) as well as EBM and CBM (Schaap et al., 2018) or multi-approach intercomparisons (Brümmer et al., 2020). Contrarily, Zimmermann et al. (2006) found a good agreement between CBM and IFM, while in the study of Thimonier et al. (2019) a throughfall based method (although not a CBM), IFM and EBM generally yielded similar rates of TIN deposition with notable exceptions at some sites. These findings suggest that comparisons of deposition estimates are most informative when carried out across a large number of sites and long observation periods.

Model intercomparisons can support the interpretation of results from single methods and indicate conditions where

TABLE 1 | Calculation approaches of total inorganic nitrogen fluxes for the different deposition pathways (DP) and methods.

DP	Name of approach		
	Canopy budget model (CBM)	**Inferential method (IFM)**	**Emission based method (EBM)**
Wet (WD)	Empirical BD to WD conversion factors for NO_3^- and NH_4^+ applied to *in situ* measurements of bulk deposition (BD)		Wet and bulk deposition measurements of NO_3^- and NH_4^+, regionalized with geostatistical methods using concentration fields from LOTOS-EUROS and precipitation fields from the German Weather Service
Dry (DD)	Modeled based on assumptions about the concentration ratios of nitrogen compounds relative to Na^+ in WD, DD, and OD. Informed by measurements of bulk open field and stand precipitation	*In situ* measurements of ambient air NH_3 and NO_2 concentrations using passive samplers combined with site specific deposition velocities. HNO_3, NO_3^-, and NH_4^+ estimated after Schmitt et al. (2005)	Chemical transport model LOTOS-EUROS
Occult (fog) (OD)		Taken from EBM	Estimated based on modeled meteorological data, concentration fields used for the WD of EBM and empirical fog water enrichment factors

specific approaches are more or less reliable. The aim of this study is to contribute a systematic comparison of three common approaches to estimate TIN deposition to forests for an extended geographic and temporal coverage. Based on data from around 100 intensive forest monitoring sites (42 sites for IFM) in Germany over a period of 16 years, we derive TIN deposition estimates with (i) the "canopy budget model" (CBM), (ii) the "inferential method" (IFM), and (iii) "emission based estimates" (EBM). We evaluate the discrepancies between the different approaches using mixed effect models in order to analyze if they are determined by spatial, temporal, meteorological, and site specific factors. Where applicable, model discrepancies were analyzed separately for wet deposition (WD), dry deposition (DD), and total deposition (TD). In this study, we hypothesize that the difference between the methods can be partly explained by meteorology, terrain characteristics, site specific factors and levels of ambient air concentrations.

MATERIALS AND METHODS

In the following subchapters a description of the assessments and models is provided. The overall study design is summarized in **Table 1**.

Study Sites and Data Coverage

In Germany, data collection under the International Co-operative Programme on Assessment and Monitoring of Air Pollutions Effects on Forests (ICP Forests) is conducted since more than two decades (Ferretti and Schaub, 2014). As part of this program, atmospheric deposition is assessed at intensive monitoring plots ("Level II") by means of precipitation sampling in the forest stands and at nearby open field sites (De Vries et al., 2003). Hundred and four sites with varying temporal coverage and a variety of forest stand types were examined for this study (**Figure 1**). The most frequent tree species is Norway spruce [34] (*Picea abies* (L.) H. Karst), followed by European beech [30] (*Fagus sylvatica* L.), Scots pine [17] (*Pinus sylvestris* L.), oak [8], (*Quercus robur* L. and *Qu. petraea* (Matt.) Liebl.), Douglas fir [1] [*Pseudotsuga menziesii* (Mirbel) Franco], European larch [1] (*Larix decidua* Mill.) and stands with more than one dominant tree species [13].

The plots are located at altitudes between 10 and 1,522 m a.s.l. Mean air temperature and mean annual precipitation (1981–2010) ranged from 2.6 to 10.9°C and from 558 to 2,444 mm, respectively. While data according to EBM approach are available for all plots and years in the period 2000–2015, application of the CBM and the IFM approach is limited by the availability, completeness and quality of observations. The CBM and IFM were calculated for 1,237 and 194 site-years, respectively. Further information on the sites and data availability is provided in the supplementary material (**Supplementary Table 1**).

Sampling Procedures, Chemical Analysis and Data Quality

Deposition assessments for the CBM approach were conducted according to the ICP Forests Manual on sampling and analysis of deposition (Clarke et al., 2016). In short, open field deposition was collected by 3–6 continuously open bulk samplers at sites in the vicinity of the forest stands. Between 9 and 27 collectors are placed under the forest canopy in varying spatial arrangements in order to cover the spatial variation in throughfall deposition. At plots with European beech, stemflow is assessed at a subset of the trees (Clarke et al., 2016). Usually, samples from multiple samplers are pooled in order to reduce the analytical effort.

Samples are collected at least fortnightly, filtered, and then stored in the dark at about 4°C or below before chemical analyses are performed. For some plots samples are mixed to monthly samples. Deposition samples were analyzed for Na^+, NH_4^+, and NO_3^-, and a range of other parameters by different laboratories. Due to the standardized methods (Clarke et al., 2016), data are comparable and laboratory results are checked with currently recommended methods (Mosello et al., 2005): (1) the ion balance, (2) a comparison between measured and calculated conductivity, (3) a comparison between the sum of the inorganic forms of nitrogen and total nitrogen, and (4) the Na/Cl ratio. If analytical results are suspicious, analyses are repeated. The QA/QC procedures further included the use of control charts for internal reference material to check long-term

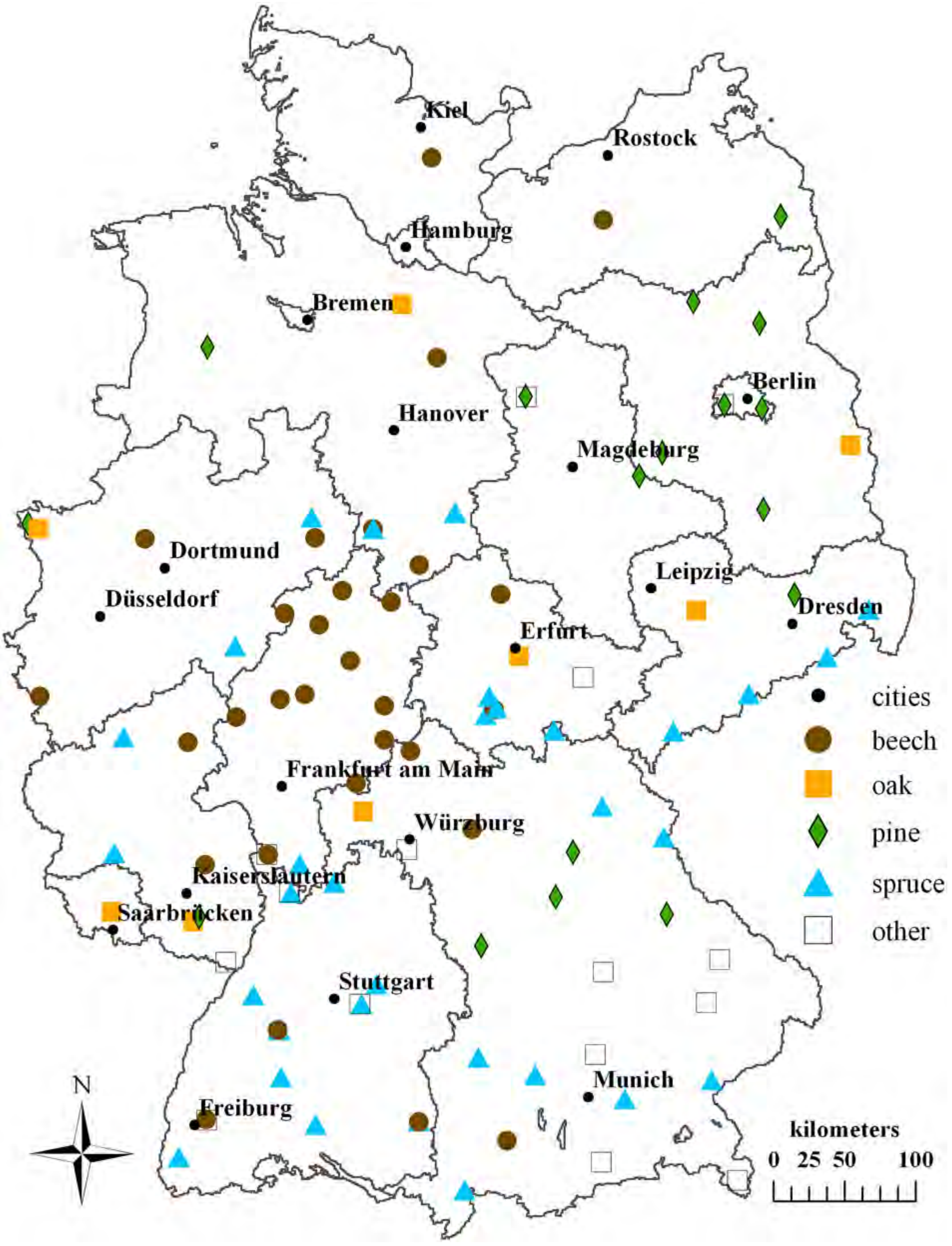

FIGURE 1 | Location of 104 German intensive monitoring plots considered in the study. Symbols representing beech, oak, spruce and pine dominated forest sites and sites with other trees (Douglas fir, larch, mixed forest).

comparability within national laboratories (König et al., 2013) as well as participation in periodic ring tests to check comparability between laboratories (Marchetto et al., 2006).

The three deposition fluxes (bulk open field, throughfall, stemflow) are then calculated by multiplication of the precipitation amount with the corresponding ion concentration in the analyzed precipitation samples and summed up to annual rates. Only annual open field and throughfall deposition fluxes, which were based on at least 292 days of collection (80% of the year) have been included. In case of data gaps (between 0 and 20% of the year), the corresponding deposition rate has been extrapolated to full temporal coverage based on the assumption that daily deposition fluxes in the unobserved time periods equal the average daily deposition fluxes in the observed period for the respective plot, sampler and year (Fischer et al., 2007). For stemflow (on average amounting to approximately 10–16% of the Na^+, NH_4^+ and NO_3^- throughfall deposition flux), longer data gaps frequently occurred. They were filled based on plot- and substance-specific average ratios between stemflow and throughfall deposition rates for those measurement periods where throughfall was available. Finally, the stand precipitation (ST) deposition flux was calculated as the sum of throughfall and stemflow for beech plots and equaled the throughfall flux for all other plots.

Ambient air concentrations of NO_2, and NH_3 were assessed at 43 sites by passive samplers in different years (**Supplementary Table 1**). Measurements were made using IVL passive samplers usually at 2 m above ground, installed in the open field where bulk open field precipitation was assessed (Schaub et al., 2016). The samples were mostly processed and analyzed by the Swedish Environment Research Institute (IVL). More details on the samplers are given in Swaans et al. (2007). All years with a data completeness of <80% for a specific air pollutant were excluded for the respective measurement site (Schaub et al., 2016).

Approaches to Estimate Total Inorganic Nitrogen Deposition

N deposition to forests consists of several N components. We refer to TIN as the substances NH_4^+ and NO_3^- (ions in precipitation and aerosols) as well as NH_3, NO_2, and HNO_3 (gases). The three approaches compared in this study cover these components to a slightly different extent. The EBM reports deposition rates for oxidized N (NO_y) which also includes compounds like HNO_2 and NO. The canopy budget model also accounts for these substances as they mostly react to N forms captured by the measurements used for the method (Thimonier et al., 2019). The canopy budget model, however, only partly covers the deposition of gases in general (see below). The inferential method explicitly models the deposition fluxes of the five TIN compounds. These differences must be taken into account for the interpretation of results. The deposition of organic N is not the specific subject of this study. In the following, the three methods are briefly described.

Canopy Budget Model

A number of CBM versions exist and differences between models were evaluated in other studies (Staelens et al., 2008; Adriaenssens et al., 2013). We selected the approach of Ulrich (1994) as a relatively robust and conservative version [the approach probably underestimates TIN TD for several reasons (Meesenburg et al., 2009), see Discussion)]. Based on the assessment of NO_3^- and NH_4^+ in bulk open field precipitation and ST, dry deposition of gaseous and particulate N species is estimated. Therefore, the sum of the calculated NO_3^- and NH_4^+ TD is referred to as TIN TD. In detail, the CBM of Ulrich (1994) calculates the TD of the nitrogen components (NC) NO_3^- and NH_4^+ as the sum of WD and interception deposition (ID):

$$TD_{NC} = WD_{NC} + ID_{NC} \tag{1}$$

Wet deposition was estimated from bulk open field precipitation based on correction factors from Gauger et al. (2002). Due to the high temporal and spatial variability of the factors, this can only be considered as a rough approximation. More details on the limitations are given in section Uncertainties in Methods and Measurements. The ID is conceptually split into (1) particulate ID ($ID_{part,NC}$), consisting of particulate DD and OD, and (2) gaseous deposition ($ID_{gas,\ NC}$).

$$ID_{NC} = ID_{part,NC} + ID_{gas,NC} \tag{2}$$

The model assumes that concentration ratios of substances (Na^+:NC) in ID_{part} are similar to concentration ratios of substances in WD. Furthermore, it is assumed that ID_{part} of sodium can be estimated as the difference of ST and WD (zero net canopy exchange of Na^+). Based on these assumptions, ID_{part} of each of the two nitrogen compounds can be estimated as:

$$ID_{part,NC} = \frac{(ST - WD)_{Na}}{WD_{Na}} \cdot WD_{NC} \tag{3}$$

The ID of gaseous N species is estimated as the share of ST that is not explained by WD or ID_{part} of NO_3^- and NH_4^+, respectively.

$$ID_{gas,NC} = ST_{NC} - WD_{NC} - ID_{part,NC} \tag{4}$$

If the sum of WD and ID_{part} exceeds ST, no gaseous deposition can be calculated (treated as zero). Finally TIN TD is calculated as the sum of TD of NH_4^+ and NO_3^-. For more details, the underlying assumptions and limitations see Ulrich (1994) or Meesenburg et al. (2009). Note that the CBM yields an estimate of ID but does not allow to differentiate between DD and OD. Therefore, the OD and DD fluxes of the other two methods (IFM and EBM, see below) are also aggregated to yield the respective ID fluxes. As the OD share among the ID is usually relatively small, and in order to reduce the complexity of the figures and tables, we present the results for OD and DD together as "dry" deposition (**Table 1**).

Inferential Method (IFM)

Calculation procedure

The inferential method (IFM, also referred to as "concentration method", e.g., Peters and Eiden, 1992), calculates the dry deposition flux (DD; g m^{-2} s^{-1}) as the product of the concentration (c; μg m^{-3}) in the ambient air at a defined reference height (z) and a proportionality constant, the deposition velocity (vd; cm s^{-1}) according to the following basic equation (Wesely and Hicks, 2000):

$$DD = v_d(z) + c(z) \tag{5}$$

Following Thimonier et al. (2019) we focused on NH_3, NO_2, HNO_3 (gases), and NH_4^+ and NO_3^-(aerosols). As *in-situ* measurements were only available for NH_3 and NO_2, the calculation of DD based on vd and ambient air concentration was only applied for these substances, which usually account for a large part of TIN DD (Flechard et al., 2011). The contribution of HNO_3, NH_4^+, and NO_3^- to DD was estimated following Schmitt et al. (2005). In detail, we proceeded as follows: (1) we obtained WD of NH_4^+ and NO_3^- in the same way as for the CBM approach (**Table 1**). (2) We then calculated the DD of $NH^+_{4,\ part}$, $NO^-_{3,\ part}$, and $HNO_{3,\ gas}$ based on an empirical relationship (Schmitt et al., 2005) from open field deposition, separately for broadleaved and coniferous forest. OD is not included here (Schmitt et al., 2005). (3) Gaseous DD of NH_3 and NO_2 was calculated by multiplying annual average ambient air concentrations with deposition velocities (see below). (4) As independent data to inform OD estimates was not available, we used the OD from the EBM approach (see below) also in the IFM approach (**Table 1**). The contribution of this deposition pathway is usually very small. (5) The TIN TD estimate of the IFM is then calculated as the sum of the deposition fluxes from steps 1–4. (6) In order to allow a separate comparison of the deposition fluxes, we subtracted WD (from step 1) from the TD (step 5). Although this flux contains small parts of OD, we refer to it as dry deposition (DD) in subsequent steps of analyses (same for the other two methods).

Estimation of deposition velocities for NO_2 and NH_3

Previous reviews of deposition velocities for different forest types and substances reported a large variability of vd values, which appeared to be sensitive to several parameters such as receptor surface properties, meteorological conditions as well as seasonal, and diurnal variations (Hunová et al., 2016). To account for this variability, we derived two sets of deposition velocities. In the standard case, we used forest type specific vd values for each substance across Germany and the complete observation period. In a second case, we used semi-empirical site and season specific correction factors following Kirchner et al. (2014), to roughly account for the major spatial and temporal variations in vd.

In order to establish the fixed "forest type specific values" of the deposition velocity, we rely on four review studies, each covering several publications. We extracted the vd values for NH_3 and NO_2 reported to be best suited (median of vd's in one case) for the respective forest type by each of the four studies. We then aggregated these four values into one value per forest type and N species by using the midrange (average of the lowest and highest value). In order to roughly account for the range of uncertainty, we also calculate "standard value+30%" and "standard value-30%" (**Table 2**).

TABLE 2 | Deposition velocities for the inferential method (cm s^{-1}).

Forest type	Species	S1	S2	S3	S4	Min	Max	SV	SV−30%	SV+30%
Coniferous		2.1	2.9	3	3.1	2.1	3.1	2.6	1.82	3.38
Broadleaved	NH_3	0.9	1.9	2.2	-	0.9	2.2	1.55	1.09	2.02
Mixed		1.2	-	2.6	-	1.2	2.6	1.9	1.33	2.47
Coniferous		-	0.25	0.4	0.4	0.25	0.4	0.33	0.23	0.43
Broadleaved	NO_2	-	0.25	0.3	-	0.25	0.3	0.28	0.2	0.36
Mixed		-	-	-	-	-	-	0.31[a]	0.22	0.4

S1–S4 refer to the four review studies [S1: Schrader and Brümmer (2014) (reported median used), S2: Staelens et al. (2012), S3: Rihm and Achermann (2016), S4: Kirchner et al. (2014) (spruce only)]. Min and max represent the range of values of S1–S4. Standard vd value (SV) is calculated as the midrange of S1-S4. SV−30% and SV+30% are chosen to roughly span the uncertainty of the SV. Remarks: [a]SV calculated from average of SV's for broadleaved and coniferous forest.

The second set of deposition velocities was based on these "forest type specific values" but adjusted by five types of site specific correction factors, proposed for spruce stands in the Bavarian Alps (Kirchner et al., 2014) and an additional correction factor to account for the relevance of other tree species elsewhere in Germany.

$$vd_{cor} = vd_{lit} \cdot k_{sea} \cdot k_{incl} \cdot k_{wind} \cdot k_{inv} \cdot k_{up} \cdot k_{tree} \tag{6}$$

with: vd_{cor}: corrected deposition velocity; vd_{lit}: "forest type specific" deposition velocity based on literature references (cf. **Table 2**) and the correction factors: k_{sea}: season; k_{incl}: slope inclination; k_{wind}: wind speed; k_{inv}: inversion weather condition; k_{up}: slope upwind and k_{tree}: tree species.

Dry deposition strongly depends on the season (Marner and Harrison, 2004; Mohan, 2016). Kirchner et al. (2014) therefore proposes the following seasonally dependent factors (k_{sea}): Spring (1.1); summer (1.2), autumn (1.0), and winter (0.8). A consideration of the different lengths of winter periods as proposed by Schmitt et al. (2005) has been omitted. The correction factor (k_{incl}) for the slope inclination (incl; %, see below for data source) is obtained according to Kirchner et al. (2014): $k_{incl} = 0.01 \times incl + 0.6$. Parameterization of k_{wind} is based on regionalized wind speed from 109 wind stations using a Leeward index according to Dietrich et al. (2019). Wind speed is known to have a strong effect on deposition fluxes (Lin et al., 1994; Gallagher et al., 1997; Erisman and Draaijers, 2003; Mohan, 2016). Based on the average wind speed in Germany at 10 m height of ∼3.4 m s^{-1}, the following classes with the corresponding correction factors were developed, assuming DD increases with wind speed due to a higher turbulence and transport into the forest: <1 m s^{-1}: 0.7; 1.0–1.9 m s^{-1}: 0.8; 2.0–2.9 m s^{-1}: 0.9; 3.0–3.9 m s^{-1}: 1.0; 4.0–4.9 m s^{-1}: 1.1; 5.0–5.9 m s^{-1}: 1.2; ≥6 m s^{-1}: 1.3. For meteorological inversions, Kirchner et al. (2014) proposed the following correction factors (k_{inv}) related to frequency of their occurrence: "rare": 1.0; frequent: 0.9; very frequent: 0.8. As no corresponding information is usually available for the investigated sites, we calculated the terrain exposure index (TEI) as predictor. The TEI is a terrain parameter, which indicates the degree to which a particular location is sheltered against advective flows and is thus particularly suitable to accumulation of cold air (Dietrich et al., 2019). The index values and correction factors are classified as follows: ≥1.2: 1.4; <1.2–≥1.1: 1.2; <1.1–≥1: 1.0; <1–≥0.9: 0.9 and <0.9: 0.8. Kirchner et al. (2014) have integrated upslope winds into their approach because they can periodically transport emissions from source regions (Benedict et al., 2013). However, the occurrence of slope upwinds and its influence on vd values (k_{up}) is difficult to parameterize. Due to the high surface roughness of forests, this effect was only considered for slopes >5°. According to Kirchner et al. (2014), north-exposed slopes are less affected than south exposed ones. Accordingly, a k_{up} factor of 1.1 was assigned for the celestial directions NW, N, NE, and E, for W and SE exposed slopes a factor of 1.2 and for SW and S exposed slopes a factor of 1.3. Vd values obtained from reviews are often stratified according to forest type (coniferous vs. deciduous). The approach by Kirchner et al. (2014) has been developed for spruce stands but only 34 of the 104 plots included in this study were pure spruce stands. The leaf area index (LAI) in spruce stands is often higher than in pine stands (Panferov et al., 2009; Goude et al., 2019). Zhang et al. (2003) found generally higher vd values for stands with higher LAI values. Corresponding, vd values for pine were assumed to be lower by a factor of 0.7 und for spruce to be 1.3 times higher compared to the "forest type specific values" for coniferous forest. For the same reasons (Bequet et al., 2011) we set a k_{tree} of 0.9 for oak and 1.1 for beech trees. For all other trees k_{tree} was set to 1.0.

Emission Based Deposition Model (EBM)

The approach for quantifying TIN deposition with the EBM is described in detail in Schaap et al. (2018). The deposition fluxes estimated by the EBM were provided by the German Environment Agency. In short, four major calculation steps are conducted in this model: (1) the chemical transport model LOTOS-EUROS (Schaap et al., 2008; Manders et al., 2017) is used to calculate DD as a product of modeled ambient air concentration fields of N species and modeled deposition velocities. Critical input data are meteorological data in high temporal resolution, spatial information of N emissions and receptor properties for dry deposition (e.g., land cover). (2) In the next step, modeled rain water concentrations from the LOTOS-EUROS model are used in combination with a few 100 stations of precipitation chemistry monitoring in Germany. These data serve to adjust the modeled rain water concentration distribution from the LOTOS-EUROS model using residual kriging. The generated concentration field is multiplied with high resolution precipitation data (1 × 1 km), to yield WD estimates (**Table 1**). (3) OD is calculated from fog water concentrations [estimated from previously determined rainwater concentration field and so called enrichment factors–Schaap et al. (2018)] in combination with cloud water deposition rates, which were calculated following the approach by Katata et al. (2008, 2011). In Katata et al. (2008) a simple linear regression for the fog deposition velocity has been derived from numerical experiments with a detailed multilayer land surface model (4) Finally WD, DD, and OD were combined in a spatial resolution of 1 × 1 km for the years 2000–2015. For each grid cell, land cover type specific deposition rates are available, including coniferous forest, deciduous forest, and mixed forest. Thus, deposition rates at the ICP Forests monitoring sites were extracted from the EBM results based on site coordinates and tree species / stand type (see **Figure 1**). In line with the CBM and the IFM approach, we refer to the sum of DD and OD estimates as "dry deposition."

Derivation of Large Scale Ambient Air Concentrations, Meteorological and Terrain Data

Differences in deposition estimates between the three approaches might be affected by a range of factors including meteorological and terrain characteristics as well as the level of ambient air concentrations. Daily data of temperature (T), solar radiation (RA), relative humidity (RH), wind speed (W), and precipitation (P) were obtained for the period from 1981 to 2015 using the observational data of the German Meteorological Service (Deutscher Wetterdienst, DWD). The regionalization of the daily meteorological data from the climate and precipitation stations of the DWD to the intensive monitoring plots was performed using the methods described in Dietrich et al. (2019). Terrain parameters [altitude, slope, aspect, terrain exposure index (TEI)] were also derived following Dietrich et al. (2019). The slope orientation of the plots was transformed into a continuous variable (aspect index) between 0 and 1 following Roberts and Cooper (1989).

Discrepancies between model estimates might also be affected by the degree of air pollution at the sites. To account for this aspect, we included the annual average NH_3 and NO_X concentrations as predictors in the statistical models. Because *in-situ* measurements were only available at the much smaller subset of plots for which the IFM approach could be calculated, we relied on modeled ambient air concentrations to provide data for all plots over the entire observation period. In order to ensure independence from the chemical transport model used in the EBM approach (LOTOS-EUROS), we utilized data from the EMEP MSC-W model (Simpson et al., 2012). Annual average air concentrations based on emissions and meteorology for the years 2000–2015 according to the 2019 reporting status

TABLE 3 | Definitions of comparison indicators [after Li (2017), adapted].

Error/accuracy measure	Definition (see explanations below)
RMSE	$\sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(y_i-\hat{y}_i\right)^2}$
Mean absolute error (MAE)	$\frac{1}{n}\sum_{i=1}^{n}\left\|y_i-\hat{y}_i\right\|$
Mean bias error (MBE)	$\frac{1}{n}\sum_{i=1}^{n}\left(y_i-\hat{y}_i\right)$
Legates and McCabe's (E_1)	$\left(1-\frac{\sum_1^n(y_i-\hat{y}_i)}{\sum_1^n(y_i-\bar{y})}\right)$
Coefficient of determination (R^2)	$\left(\frac{\sum_1^n(y_i-\bar{y})\left(\hat{y}_i-\hat{\bar{y}}_i\right)}{\left(\sum_1^n(y_i-\bar{y})^2\left(\hat{y}_i-\hat{\bar{y}}_i\right)^2\right)^{1/2}}\right)^2$

n, number of observation years; y_i, the values according to first method; $\hat{y}_i$, the values according to second method; $\bar{y}$, mean of the first method values; and $\hat{\bar{y}}_i$, mean of the second method values.

TABLE 4 | Summary of data sources for explanatory variables in the statistical models to analyze the differences in TIN deposition between the three approaches.

Variables	Description reference	Source	Minimum	Median	Maximum	Unit
Site and terrain characteristics						
EAST	East position of the site	ICP forests	3,297,187	3,566,278	3,888,468	GK3[a]
NORTH	North position of the site	ICP forests	5,271,504	5,590,156	5,997,172	GK3[a]
ALT	Elevation above sea level	ICP forests	10	458	1,522	m a.s.l.
TREE	Tree species	ICP forests				Factor
SLOPE	Slope inclination	DEM[b]	0	3	24	Degrees
ASPECT	Orientation of slope	DEM[b]	26	187	330	Degrees
ASPINDEX	Index from aspect	calculated	0.00	0.49	1.00	
TEI	Terrain exposure index	DEM[b]	0.89	1.09	1.27	Index
Annual meteorology and air quality data in the period from 2000 to 2015						
T	Annual mean air temperature	DWD[c]	1.8	8.6	12.4	°C
P	Annual precipitation sum	DWD[c]	380	908	2790	mm
RH	Annual mean relative humidity	DWD[c]	70.2	81.7	89.7	%
RA	Annual solar radiation sum	DWD[c]	3,163	3,917	4,893	$MJ\ m^{-2}$
WIND	Annual mean wind speed	DWD[c]	1.4	2.6	4.1	$m\ s^{-1}$
NO_X	Annual mean NO_X concentration	EMEP	0.6	2.8	11.1	$\mu g\ m^{-3}$
NO_3	Annual mean NH_3 concentration	EMEP	0.3	1.5	12.0	$\mu g\ m^{-3}$
YEAR	Year of measurement	ICP Forests	2000	2007.5	2015	-

These values are valid for CBM and EBM comparison (maximum range).
[a]Gauss–Krüger system; [b]Derived from the digital elevation model (DEM) with SAGA; [c]regionalized from daily observations of the National German Weather Service (DWD) following Dietrich et al. (2019).

were obtained from EMEP MSC West (MET Norway; https://emep.int/mscw/mscw_moddata.html). Data was extracted for the grid cells in which the ICP Forests monitoring sites are located.

Statistical Analysis of Spatial and Temporal Differences Between the Methods

We compared the three model types with summary statistics. For the IFM, we used the version with site specific correction factors vd_{cor}. We also tested a version with site specific correction factors but excluding the tree species-specific correction (k_{tree}) and another version with the forest type specific vd only. To quantify the statistical association between the estimated deposition rates from the different methods, the root mean square error (RMSE), as well as the mean bias error (MBE), the mean absolute error (MAE), the coefficient of determination (R^2) and Legates and McCabe's efficiency (E_1) were used (**Table 3**). The E_1 (Legates and McCabe, 2013) provides additional information with $E_1 = 1$ indicating a perfect fit while $E_1 = 0.0$ indicates a model that is no better than the baseline comparison (the observed mean value—Null model). Substantially flawed results are indicated by negative E_1 values (Legates and McCabe, 2013).

We used a mixed effect model to relate the differences between deposition estimates ($\Delta TIN_{y,p}$) from the three approaches to potential explanatory factors taking into account the "pseudo-replicated" structure of the data (same plots in different years) (Zuur et al., 2009). The model structure is as follows:

$$\Delta TIN_{y,p} = b_0 + f_1\left(x_{1,yp}\right) + f_2\left(x_{2,yp}\right) + \ldots + f_n\left(x_{n,yp}\right) + Z_p b_p + \varepsilon_{yp} \tag{7}$$

were $\Delta TIN_{y,p}$ is the difference in TIN deposition in year y at plot p; b_0: the intercept term; $f_1, f_2,...f_n$: unspecified (potentially) non-linear spline smoothing functions; $x_{1,yp}, x_{2,yp},...,x_{n,yp}$: 1... *n* predictor variables in year y at plot p; Z_p: a row in a model matrix including dummy variables for coding random effects for plots *p*, where $p = 1,...,104$; b_p: a vector of random effects; ε: an independent and identically normally distributed error term with standard deviation e_{yp}. Standard software to parameterize this type of model is available from the R (R Development Core Team, 2018) library mgvc (Wood, 2006), with additional calls to the libraries MASS (Venables and Ripley, 2003) and nlme (Pinheiro et al., 2018). The distribution of the response variable was checked with the function "fitdist" of the package "fitdistrplus v1.0-14" (Delignette-Muller and Dutang, 2015). In case of data deviating from normal distribution, logarithmic or square root transformations were performed with constants added where necessary to avoid negative values.

All explanatory variables are summarized in **Table 4**. It should be noted that some of these variables (e.g., wind speed) are already included in the semi-empirical factors for IFM. Therefore, significant effects of these parameters could also indicate deficient parameterization of the IFM. We used high-resolution regionalized climate data instead of precipitation observations at the intensive monitoring

TABLE 5 | Descriptive statistical values of the three approaches for estimation of total inorganic nitrogen (TIN) deposition (canopy budget–CBM; inferential method–IFM; emission based–EBM) for the different deposition pathways [wet deposition (WD), dry deposition (DD), and total deposition (TD)].

Approach	Deposition Pathway	Mean kg ha^{-1} a^{-1}	Median kg ha^{-1} a^{-1}	Min kg ha^{-1} a^{-1}	Max kg ha^{-1} a^{-1}	sd kg ha^{-1} a^{-1}	cv [%]
Sites with CBM and EBM TIN deposition (1,237 site-years)							
CBM	WD	8.5	8.2	2.2	23.5	2.8	33
	DD	11.5	10.6	0.0	37.7	5.8	50
	TD	20.0	19.0	6.1	47.1	7.1	36
EBM	WD	9.3	8.7	3.3	22.6	2.9	31
	DD	8.7	8.3	2.7	20.3	2.5	29
	TD	18.0	17.3	8.8	36.8	4.8	26
Sites with IFM, CBM, and EBM TIN deposition (194 site-years)							
CBM	WD	9.1	8.7	3.6	18.6	2.4	26
	DD	12.6	11.8	3.8	45.8	5.9	47
	TD	21.6	21.0	7.8	53.7	7.2	33
IFM[a]	DD	12.9	12.0	1.0	29.4	5.4	42
	TD	21.9	21.3	8.4	41.7	6.6	30
EBM	WD	9.6	9.2	4.6	18.0	2.6	27
	DD	9.3	8.4	6.3	19.2	2.6	28
	TD	18.9	17.6	12.2	33.6	4.8	25

Sd = standard deviation, cv = coefficient of variation.
[a]WD adopted from CBM.

plots as explanatory variables for the statistical models. This allows us to keep explanatory variables independent from input data of the three methods we aim to compare. To identify the factors that influenced the differences in deposition estimates between the three approaches, we used a boosting framework called component-wise gradient boosting (Mayr et al., 2017), implemented in the R-package mboost (Hothorn et al., 2020). The preselection of potentially appropriate model variables takes into account parametric, non-parametric, spatial, and random effects (Bühlmann and Yu, 2003; Bühlmann and Hothorn, 2007). In mboost, the major tuning parameter of boosting is the number of iterations "mstop." To prevent overfitting, we used the implemented k-fold cross validation function to choose an appropriate number of boosting iterations. For the final model selection, we fitted the generalized additive mixed models (GAMM) with the preselected variables from the mboost procedure. Finally, all variables with a very low accumulated in-bag risk reduction (these values can be used to reflect variable importance) and non-significant ($p < 0.05$) effects were then stepwise removed from the model.

RESULTS

Magnitude and Variability of Total Inorganic Nitrogen Deposition

For the 1,237 annual observations considered in our study, the TIN TD averaged over time per plot ranges between 6.1 and 47.1 kg ha^{-1} a^{-1} and between 8.8 and 36.8 kg ha^{-1} a^{-1} with a mean of 20 and 18 kg ha^{-1} a^{-1} and a coefficient of variation of 36 and 26% for CBM and EBM, respectively (**Table 5**). There was considerable variation in estimated DD for the CBM approach. The coefficient of variation calculated across all stands and years was 50%. As expected the data of the EBM approach shows a clearly lower variability (29%).

Comparison of the Canopy Budget and the Inferential Method

Since both methods use identical observations of WD, the comparison focuses on dry and total deposition. For both dry and total deposition, the use of forest type specific vd values without further corrections shows a large dispersion and discrepancy (E_1, RMSE, MAE) between the two methods and the bias is relative high (**Figure 2**, **Table 6**). When site specific correction factors are taken into account, the agreement between the two methods considerably improves. The R^2 is relatively high, the E_1 rises substantially above zero, the RMSE and MAE are about halved, and also the MBE is low (-0.3 kg ha^{-1} a^{-1}) for TD estimates (**Table 6**).

Comparison of the Canopy Budget and the Emission Based Method

Estimates for the comparison of the CBM and EBM approaches are available for a large set of plots and years (**Table 6**, **Figure 3**). There is an overall good agreement ($R^2 = 0.47$) between CBM and EBM estimates for WD (**Figure 3A**). On average, the wet-only corrected TIN bulk deposition (CBM) is 0.8 kg ha^{-1} a^{-1} lower than WD from EBM (**Table 6**). For DD, large discrepancies between CBM and EBM appeared ($R^2 = 0.02$; $E_1 = -0.05$, **Figure 3B**). However, the bias of 2.8 kg N ha^{-1} a^{-1} is lower than for the EBM-IFM comparison (bias of 3.3 kg N ha^{-1} a^{-1}). Due to the weak agreement of the DD estimates, the association between

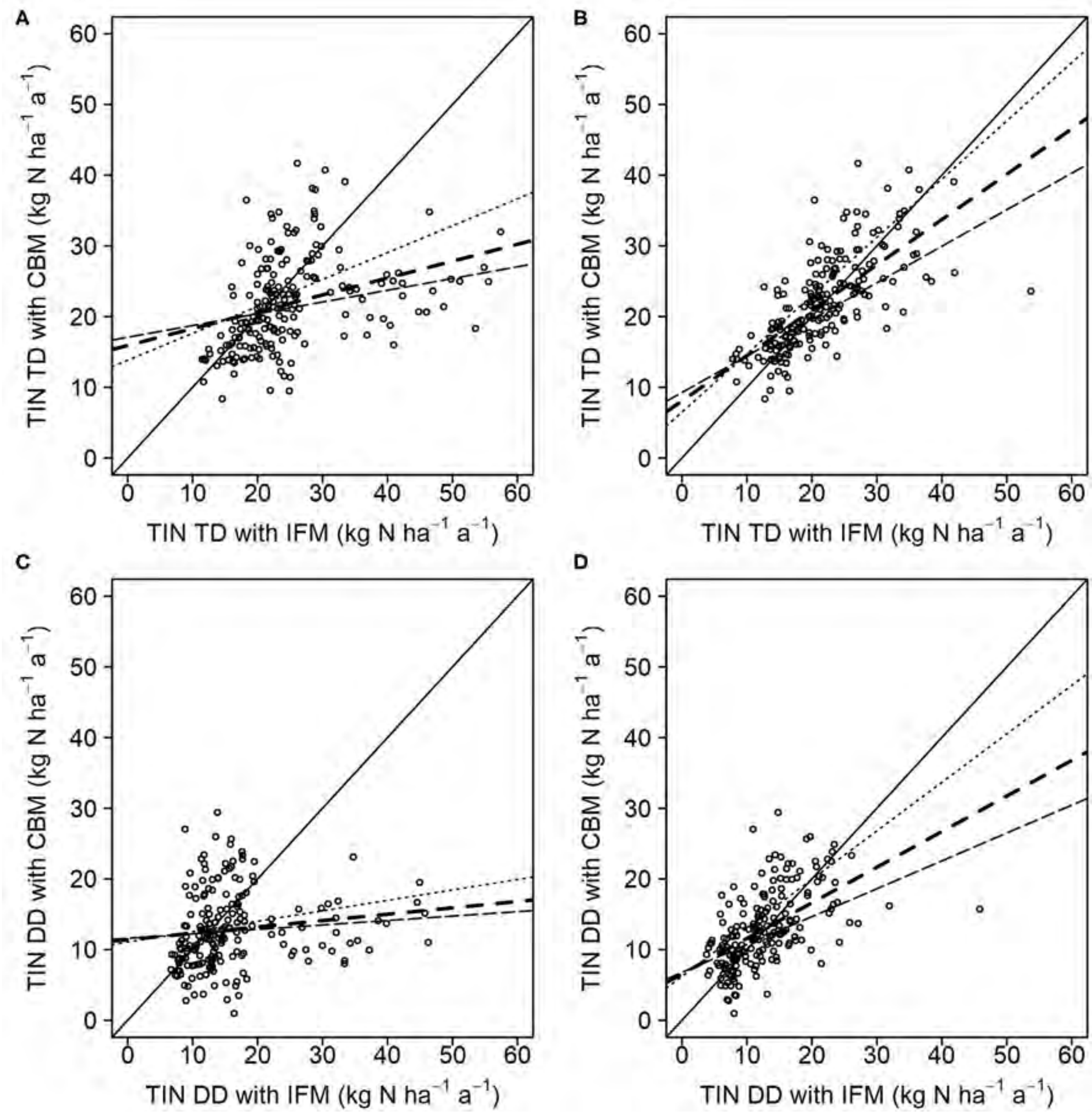

FIGURE 2 | Comparison of total deposition (TD) **(A,B)** and dry deposition (DD) **(C,D)** of total inorganic nitrogen (TIN) between canopy budget (CBM) and inferential method (IFM) ($n = 194$ site-years from 42 sites). **(A,C)** calculated with forest type specific deposition velocities; **(B,D)** calculated with site specific deposition velocities. The solid black line represents the 1:1 line and the dashed lines represents the linear regressions lines for vd_{mean} (- - - -), vd_{min} (····), and vd_{max} (— —–) (see also **Table 2**). For vd_{min} and vd_{max} only the regression lines were displayed and not the individual points. All statistical parameters are given in **Table 6**.

the TD with $R^2 = 0.16$ is also very weak (**Figure 3C**). The TIN TD calculated with EBM is lower on average by 2 kg N ha^{-1} a^{-1} compared with CBM. To compensate for interannual variability, also plot-specific mean values were compared (**Figure 3D**). Using this aggregated values, the regression line approaches more closely the 1:1 line.

Comparison of the Inferential and the Emission Based Method

When comparing the wet-only corrected bulk open field deposition of the reduced dataset (i.e., only for those plots where IFM estimates are available) to WD of the EBM approach, the mean bias error (MBE) is slightly lower (−0.6 kg N ha^{-1} a^{-1}) compared to the complete dataset (**Figure 4E** and **Table 6**). In contrast, the DD from the IFM clearly shows higher values if calculated with site specific correction factors, compared to EBM (3.3 kg ha^{-1} a^{-1}, **Figure 4B**). As MBE of WD and DD compensate each other partly, the overall difference between the TIN TD estimates amounts to 2.7 kg N ha^{-1} a^{-1}. If IFM is calculated only with forest type specific deposition velocities, the association with the EBM approach is significantly deteriorated (**Figure 4** and E_1 values in **Table 6**). For this version, the MBE increases to 6.9 and 6.3 kg N ha^{-1} a^{-1} for DD and TD, respectively.

TABLE 6 | Indicators for the association between canopy budget (CBM), inferential (IFM) and emission based method (EBM).

V	DP	E_1	R^2	RMSE	MAE	MBE	*N*
				kg ha^{-1} a^{-1}	kg ha^{-1} a^{-1}	kg ha^{-1} a^{-1}	
Association between IFM and CBM							
FT	DD	−0.14	0.02	10.1	6.7	3.3	194
SI	DD	0.14	0.31	5.3	3.9	−0.3	194
FT	TD	0.01	0.12	10.1	6.7	3.3	194
SI	TD	0.30	0.49	5.3	3.9	−0.3	194
Association between CBM and EBM							
-	WD	0.20	0.47	2.4	1.8	−0.8	1,237
-	DD	−0.05	0.02	6.6	4.8	2.8	1,237
-	TD	0.08	0.16	7.1	5.2	2.0	1,237
Association between IFM and EBM							
-	WD	0.11	0.42	2.1	1.6	−0.6	194
FT	DD	−0.19	0.33	10.3	7.0	6.9	194
SI	DD	0.10	0.35	5.8	4.0	3.3	194
FT	TD	−0.01	0.30	10.3	6.8	6.3	194
SI	TD	0.21	0.43	6.1	4.4	2.7	194

V, version of IFM; FT, forest type specific deposition velocities, SI site specific deposition velocities; DP, Deposition pathway with dry deposition (DD) and total deposition (TD), Legates and McCabe's efficiency (E_1), the coefficient of determination (R^2), root mean square error (RMSE), mean absolute error (MAE), the mean bias error (MBE), and the number of site-years (N). RMSE, MAE, and MBE are identical for DD and TD because identical WD is used for the CBM and the IFM. The differences between the methods were calculated in the following arrangements. IFM-CBM; CBM-EBM and IFM-EBM. For example, a positive MBE for IFM-CBM indicates a higher TIN deposition estimates of the IFM compared to the CBM.

Factors Influencing the Difference Between N Estimation Methods

The differences between the annual TIN fluxes calculated with the three methods were examined for possible influences of spatial, temporal, meteorological and relief factors. For each combination of models (CBM, IFM, EBM) and deposition pathway (WD, DD, TD) the best model as identified by the boosting procedure for variable selection is indicated in **Table 7**. The cross-comparison of the approaches is hindered by the unequal number of replicates. While 1,237 data points (deposition rates for specific plots-years) are available for the CBM-EBM comparison, only 194 are available for the IFM-EBM and IFM-CBM comparison, respectively. This is due to the limited number of available *in-situ* ambient air concentration measurements, which are required for the IFM approach. This means that differences in effects found for the CBM-EBM and the IFM-EBM comparisons, respectively, could be either caused by the difference in the amount and identity of input data or by the difference in methods (CBM, IFM). In order to evaluate this aspect, we repeated the analyses (GAMMs) for the CBM-EBM comparison, including only those observations, which are available for the IFM/EBM comparison (n = 194) (**Table 7**). When comparing the results, the different spatial coverage must be taken into account. For example, there are no measurements of ambient NO_2 and NH_3 concentrations available from Bavaria. With the exception of slope inclination, orographic parameters do not actually appear in any of the models.

There are several significant effects on ΔTIN in the different models with varying effect strength. In the following, mainly effects with a high effect strength will be addressed, since they contribute most to the explained variance of the differences between the models. For example, in the CBM-EBM comparison the effect strength for precipitation is between 2 and −6 kg ha^{-1} a^{-1} (**Figure 5A**) whereas for the year of measurement this range is only about 1.5 kg ha^{-1} a^{-1} (**Figure 5E**, note the logarithmic scale). The ΔTIN values for WD between CBM and EBM can only be explained to a small extent by the variables included in our analyses (R^2 = 0.36). The variables with the largest explanatory power are precipitation (**Figure 5A**) and the location of the plots (**Figure 6**). The greater the amount of precipitation, either the EBM approach seems to systematically overestimate WD or the measurements of open field deposition used in the CBM and IFM are too low.

In addition, higher TIN WD rates by the EBM approach can also be observed in northwest Germany (**Figure 6A**). In contrast, somewhat lower WD rates are estimated by the EBM compared to open field measurements in northeast and southwest Germany (**Figure 6A**). Note that positive effects indicate a tendency for higher TIN deposition estimates of the CBM as compared to the EBM (**Figures 5**, **6**).

For the comparison of CBM and EBM with respect to dry deposition estimates a larger number of influential variables were identified than for WD. With increasing temperature, wind speed and slope inclination, the difference of DD estimates between EBM and CBM tends to increase (**Figure 5**). A relatively high sensitivity on ΔTIN is indicated for the partial effect of tree species (**Figure 5F**). While the differences are insignificant for all other tree species, they are significant for spruce forests (**Table 7**). In contrast to WD, the spatial trends for DD are only weak (**Figure 6B**). Similarly, the temporal effect is only poor. However, especially since 2012, there has been a slight downward trend, i.e., a tendency for higher values of the EBM compared to the CBM (**Figure 5E**).

For the comparison of the TIN total deposition between the IFM and the CBM (possible for 194 plot-years), the variable selection algorithm suggested the location of plots and tree species as the sole potentially relevant explanatory variables. However, these effects turned out to be insignificant in the GAMM, with a corresponding low explanatory power ($R^2 = 0.12$).

As for the CBM-IFM comparison, the IFM-EBM comparison was also limited to the 194 plot-years with observed ambient air quality (**Figure 7**). For WD, the statistical model identified year of measurement and a spatial effect as explanatory variables. In contrast to the comparison of CBM and EBM a significant effect of precipitation rates was not found. It should be noted that there are only very few stations with very high annual precipitation rates in the IFM subset of plots, e.g., the Bavarian Alps are missing. Although a precipitation effect on differences

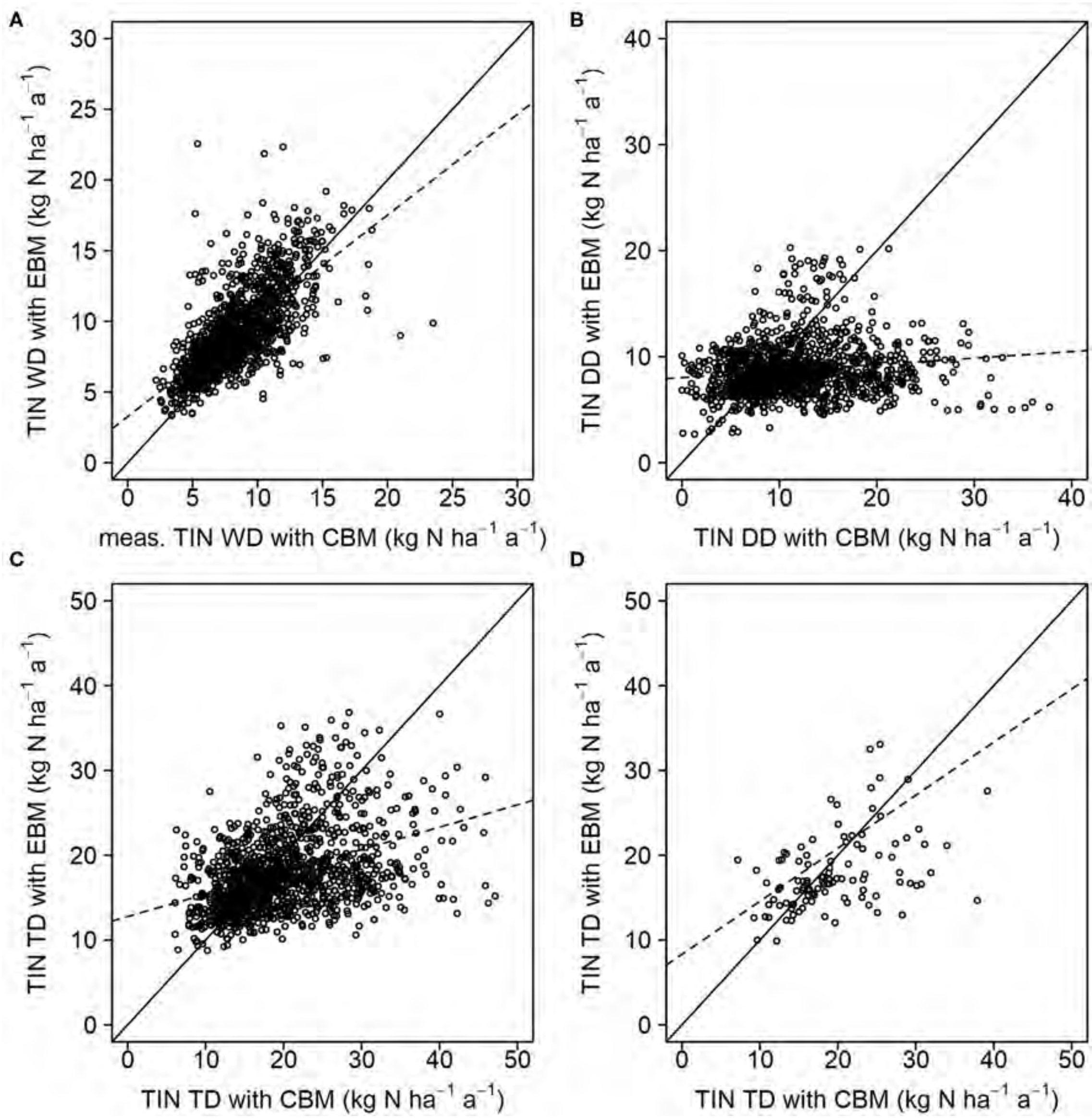

FIGURE 3 | Comparison of yearly wet deposition (WD) **(A)**, dry deposition (DD) **(B)**, and total deposition (TD) **(C)** of total inorganic nitrogen (TIN) between emission based (EBM) and canopy budget method (CBM) (n = 1,237 site-years from 104 sites). **(D)** TD with site-specific mean values. The solid black line represents the 1:1 line and the dashed line represents the linear regressions line. All statistical parameters are given in **Table 6**.

in WD was invisible, the statistical model identified a tendency for higher TD estimates of the EBM compared to IFM for plot-years with high regionalized precipitation rates. Another effect identified for the IFM-EBM comparison is a systematically lower TIN DD estimate of EBM compared to the IFM for spruce sites (**Figure 7E**). This effect of tree species is in agreement with the results of the larger set of plots used for the EBM-CBM comparison (see above). The IFM-EBM comparison also indicates an effect of solar radiation, NO_x and NH_3 air concentrations (based on data from the EMEP model) for dry deposition. However, the prognosis intervals show a high uncertainty. The comparison of the IFM and EBM methods does not reveal any spatial pattern for TD, which is likely due to the limited sample size.

In summary, main findings are:

- Similar effects found for DD estimates in the CBM-EBM (n = 1,237) and the IFM-EBM (n = 194) comparison for spruce plots. Here, the EBM tends to lower TIN DD estimates. Both CBM and IFM show this tendency, either with or without tree species specific correction (see IFM variant VT), when compared to the EBM.
- The effects of the different meteorological and air concentration variables differ between model comparisons of

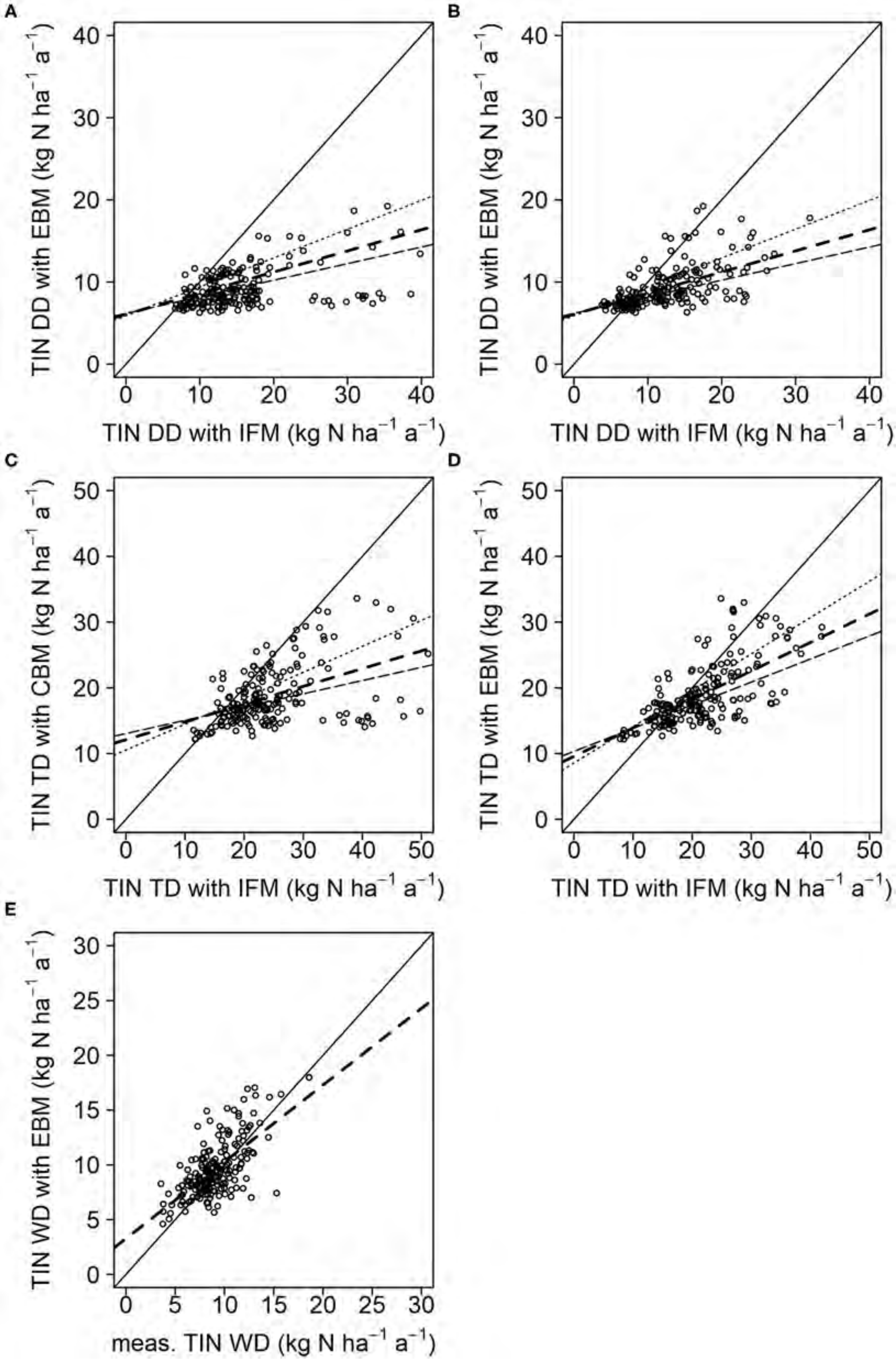

FIGURE 4 | Comparison of dry deposition (DD) **(A,B)**, total deposition (TD) **(C,D)** and wet deposition (WD) **(E)** of total inorganic nitrogen (TIN) between emission based (EBM) and inferential method (IFM) (n = 194 site-years from 42 sites). **(A,C)** calculated with forest type specific deposition velocities; **(B,D)** calculated with site specific deposition velocities. The solid black line represents the 1:1 line and the dashed lines represents the linear regressions lines for vd_{mean} (- - - -), vd_{min} (····), and vd_{max} (— —–) (see also **Table 2**). For vd_{min} and vd_{max} only the regression lines were displayed and not the individual points. All statistical parameters are given in **Table 6**.

the respective variants (**Table 7**). For example solar radiation is significant for IFM-EBM but not for the other variants. However, this can also be an effect of the limited sample size. It can be seen for TD, that when comparing CBM and EBM (n = 1,237), all variables listed in the table are significant, with the exception of solar radiation.

- Spatial and temporal effects are mainly shown for the comparison between CBM and EBM. This is likely also the result of the much larger sample size. Spatial effects with a large effect strength are mainly apparent for WD.
- With the exception of slope inclination, orographic parameters do not actually appear in any of the models.

DISCUSSION

We compared three commonly used models for the estimation of TIN deposition to forests: a canopy budget model (CBM, Ulrich, 1994), the inferential method (IFM) based on observations of ambient air concentrations and an emission-based-approach (EBM) using a chemical transport model (LOTOS-EUROS). The relatively large number of plot-years included in this study allowed us to identify general patterns of differences between the three approaches. At the same time, the amount of data made it impossible to analyze each plot-year in detail. Therefore, although several important explanatory variables were included in the statistical models, some patterns occurring at specific subsets of the data might not be well-represented in the results. The discussion comprises two main sections: (1) uncertainties in methods and measurements; (2) comparison of TIN deposition estimates between the three methods.

Uncertainties in Methods and Measurements

The three methods to estimate TIN deposition compared in this study (CBM, IFM, and EBM) are frequently applied because they can be used with relatively low effort compared to methodologically advanced micrometeorological methods. This also implies, however, that each method suffers from substantial limitations. Ellermann et al. (2018) estimated the uncertainty on nitrogen deposition for Danish land areas to be 27–43%. They interpret the high uncertainty as a result of partial uncertainties of the various N species that contribute to TIN TD. In this study, the uncertainty of the different methods can only be quantified very roughly, as the results are obtained from a combination of measurements and models with different input data and many assumptions. The following aspects of uncertainty for the three models should be considered when interpreting the results.

For WD measurements alone, uncertainties of 10–40% can be assumed due to errors in sampling and analysis (Zimmermann et al., 2006). The higher small-scale variability in forest stands is taken into account by a higher number of collectors, therefore the uncertainty in throughfall deposition is expected to be of comparable, but potentially somewhat larger, magnitude. A further uncertainty results from the application of uniform conversion factors to convert from bulk to wet deposition. These factors do not only affect wet deposition, but also the

TABLE 7 | Significance and direction of the effects explaining differences between TIN deposition estimates for different deposition pathways (DP) and pairs of models.

DP	N	ΔTIN models	C	Y	TR	P	T	RH	RA	W	S	NO_X	NH_3	R^2
WD	1237	CBM-EBM	***	~***		↓***	↑*	↑***		↑**		↑*		0.36
WD	194	CBM-EBM	***	~*										0.45
DD	1237	CBM-EBM	*	~***	↑sp***		↑**	(↑)*		↑*	↑**			0.36
DD	194	CBM-EBM			↑sp***									0.22
TD	1237	CBM-EBM	***	~***	↑sp***↑mi*	↓***	↑**	↑***		↑***	↑***	~**	~***	0.47
TD	194	CBM-EBM	**		↑sp***↑mi*					↑**		~**		0.55
DD	194	IFM-CBM	n.s.		n.s.									0.12
TD	194	IFM-CBM	n.s.		n.s.									0.12
WD	194	IFM-EBM	***	~*										0.45
DD	194	IFM-EBM			↑sp***		↓**		↑***			↓**	↑***	0.32
DD	194	IFM_{VT}-EBM	**		↑sp***↑pi*				↑***			↓**		0.50
TD	194	IFM-EBM			↑sp***	↓***						↓**		0.17
TD	194	IFM_{VT}-EBM			↑sp***↑pi*	↓***						↓**		0.15

R^2, adjusted coefficient of determination (R^2); N, number of site-years. Asterisks indicate significance levels ($p < 0.05$, **$p < 0.01$, ***$p < 0.001$, n.s., not significant but included in model, see Materials and Methods). Blank fields indicate that the parameter has not been considered relevant by the variable selection algorithm (mboost) or that it was not significant in final mixed effect models. Parameters that were not included in any model are not listed.*

ΔTIN model = Combination of models for which differences in TIN deposition estimates are analyzed; C = coordinates (easting and northing, Gauss-Krüger); Y: year of deposition data (measurement or estimated); TR = tree species (sp = sig. differences for spruce; pi = sig. differences for pine; mi= sig. difference for mixed stands). Effects must be interpreted relative to deciduous forest; P, annual precipitation sum, [mm]; T, annual mean temperature, [°C]; RH, annual mean relative humidity, [%]; RA, annual solar radiation sum, [MJ m^{-2}]; W, annual mean wind speed, [m s^{-1}]; S, slope inclination, [°]; NO_X, NO_X concentration, [μg N m^{-3}]; NH_3, NH_3 concentration, [μg N m^{-3}]; VT, variant without tree species specific correction; ↑, increasing (not necessarily linear) difference between models with increasing parameter value; ↓, decreasing (not necessarily linear) difference between models with increasing parameter value; ∼, multi-directional effect (e.g., first increasing, then decreasing).

results of the CBM method and the estimation of particulate deposition from observed wet deposition for the IFM method. The national average values we used (0.95 for NH_4^+, 0.9 for NO_3^-) have a standard deviation of 0.25 and 0.22 for NH_4^+ and NO_3^-, respectively. They are based on 79 (NH_4^+) and 86 (NO_3^-) plot-years of parallel wet and bulk sampling across Germany (Gauger et al., 2008). Bulk to wet conversion factors can vary greatly between regions and are particularly uncertain for ammonium, where losses from bulk collectors have been reported (Stedman et al., 1990; Fürst, 2016). The canopy budget model is also affected by the wet-only conversion for sodium (tracer substance in the CBM). We used the national average of 0.81 for Na^+, but the spatio-temporal variability for this value across Germany is very high (standard deviation = 0.2; Gauger et al., 2008). Further studies are required to identify variables that could explain the spatio-temporal variability and could accordingly allow for a regionalization of the conversion factors.

The CBM approach according to Ulrich (1994) relies on the robust measurements of six flux rates (Na^+, NH_4^+, NO_3^- for both open field and stand precipitation). While other canopy budget

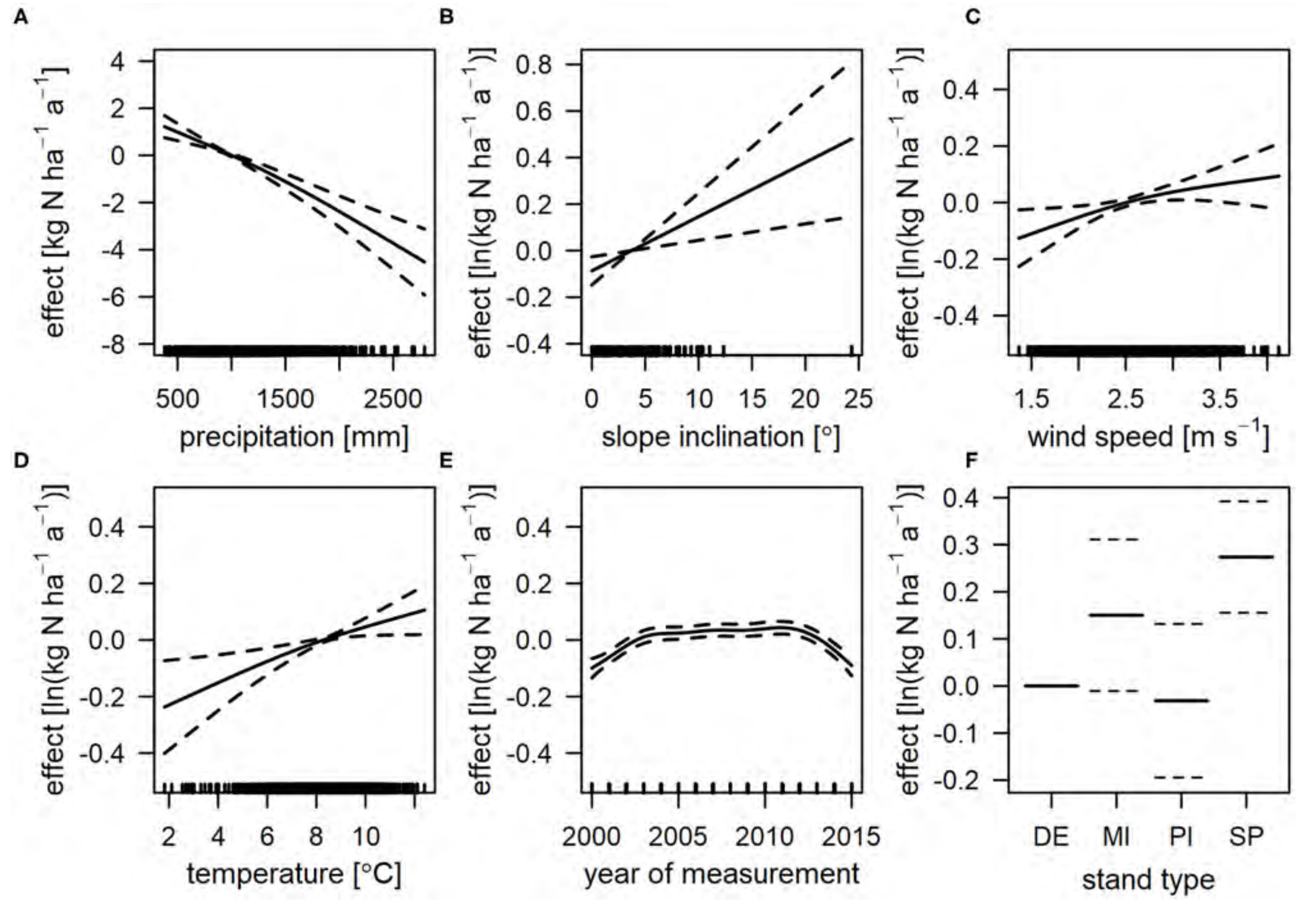

FIGURE 5 | Partial effect of precipitation **(A)**, slope inclination **(B)**, wind speed at 2 m height **(C)**, temperature **(D)**, year of measurement **(E),** and stand type **(F)** on ΔTIN between the canopy budget (CBM) and emission based method (EBM) for wet deposition **(A)** and dry deposition **(B–F)**. Positive effects indicate a tendency for higher TIN deposition estimates of the CBM compared to the EBM. Note the log-transformed data for dry deposition. Dashed lines indicate 95% pointwise prognosis intervals. The covariate is displayed as marks along the x-axis. (DE, deciduous forest; MI, mixed forest; PI, pine forest; SP, spruce forest).

models (Draaijers and Erisman, 1995; De Vries et al., 2001) require even more parameters and assumptions, the accurate monitoring of these fluxes is still challenging. Contamination with biological material can alter the composition especially of throughfall and stemflow, which is sometime challenging to detect despite the rigorous QA/QC rules applied (Mosello et al., 2005). Furthermore, the CBM approach relies on the assumption of similar concentration ratios (NH_4^+:Na^+ and NO_3^-:Na^+) in interception deposition and wet deposition. It has primarily been formulated for areas where cloud water droplets dominantly contribute to interception deposition and where substantial amounts of the airborne tracer substance (Na^+) are present (Ulrich, 1994). Deviations from these conditions are expected for the majority of the German intensive monitoring plots. The resulting uncertainties in deposition estimates remain to be investigated. Comparisons between micrometeorological methods and CBM have reported high deviations (Gallagher et al., 1997; Mohr et al., 2005). Another weakness of the CBM approach according to Ulrich (1994) is that it conceptually underestimates TIN DD as net uptake of TIN in the canopy compensates DD fluxes. Uptake of TIN in the canopy may occur via stomatal uptake of gaseous N species by the trees or via ion exchange. The conversion of inorganic to organic N species by microorganisms in the canopy additionally contributes to the underestimation of TIN DD. Canopy budget models with explicit parameterization of canopy uptake (Draaijers and Erisman, 1995; De Vries et al., 2001) estimate on average higher TIN deposition rates (Mohr et al., 2005).

Flechard et al. (2011) demonstrated that discrepancies between N deposition estimates from different IFM models at one site can be several times larger than between sites. One possible reason for this is that the IFM approach usually is a combination of observations and modeling with numerous assumptions. This also applies to the IFM approach used in our study. The gaseous components NO_2 and NH_3 were assessed at the intensive monitoring sites. The accuracy level of these measurements is stated to be about ±30% (Schaub et al., 2016). Other aspects, such as the low sampling frequency of passive samplers may cause biased results (Schrader et al., 2018).

A probably larger uncertainty is harbored in the parametrization of deposition velocity vd. Several mechanistic models for vd exist, which e.g., utilize detailed information

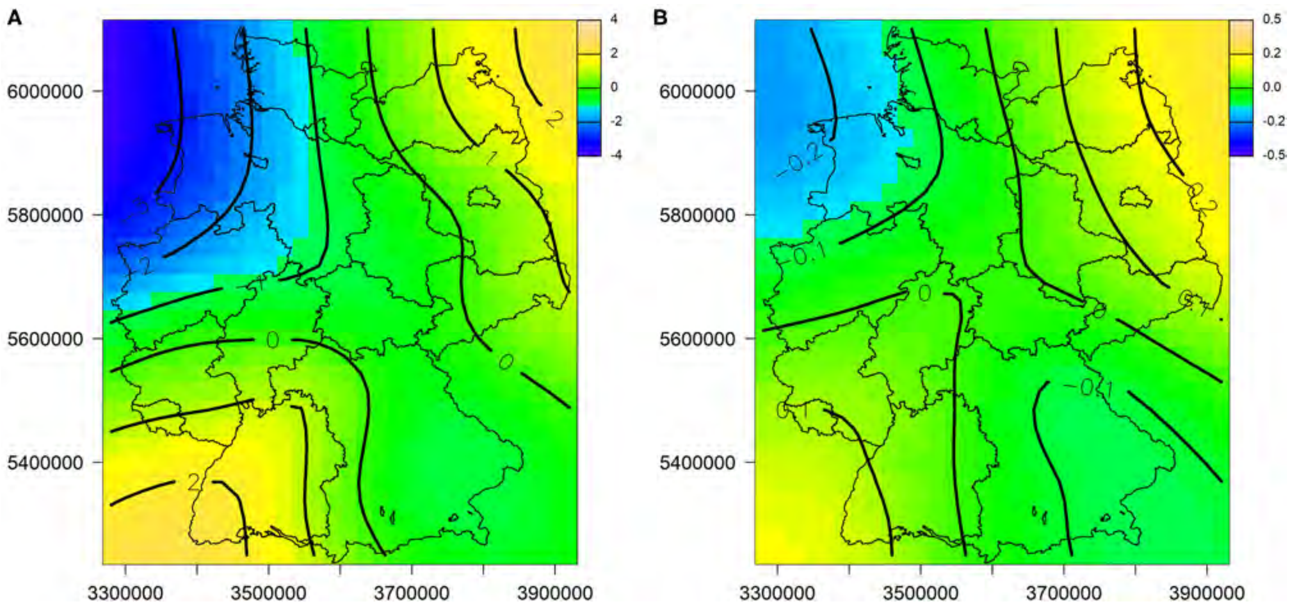

FIGURE 6 | Partial effect of geographic location on ΔTIN between the canopy budget and emission based method for wet deposition **(A)** and dry deposition **(B)**. Positive effects indicate a tendency for higher TIN deposition estimates of the CBM compared to the EBM. The values along the isolines indicate the impact on ΔTIN in kg ha^{-1} a^{-1} on the left and on ΔTIN in ln(kg ha^{-1} a^{-1}) on the right side. The axes represent Gauss-Krüger coordinates.

on meteorology and soil water availability to model stomatal opening. This allows for the parametrization of stomatal exchange if ambient air concentrations compared to foliar concentrations are known (Wichink Kruit et al., 2012). While the complexity of these comprehensive models offers the opportunity for an accurate quantification of dry deposition fluxes, additional uncertainty arises from assumptions about input parameters. We chose a different approach, starting from typical deposition velocities from the literature ("forest type specific values"). These forest type specific values were adjusted using the most important determinants for vd in order to derive "semi-empirical correction factors." The results show a much better agreement with the two other methods (CBM, EBM) than the uncorrected version. In order to account for other tree species at a majority of the intensive forest monitoring sites in Germany, we extended the IFM approach established by Kirchner et al. (2014) at 9 spruce sites in the Bavarian Alps by the tree species specific correction term. This extension and the use of the terrain exposure index (TEI) as a proxy for the frequency of inversion weather conditions were the only modifications made. Applying these semi-empirical correction factors reduced the bias between the IFM and both the EBM and the CBM approach substantially (**Table 6**). Additionally, in order to illustrate the uncertainty caused by the forest type specific deposition velocity values, the results for 30% higher and lower vd, which roughly corresponds to the variability of vd from the literature, were integrated as regression lines (**Figures 2**, **4**).

Since the deposition of gaseous HNO_3 and particulate NO_3^- and NH_4^+ often only accounts for a small proportion of dry deposition (Thimonier et al., 2019) and no observations are available, we used an empirical relationship (Schmitt et al., 2005) which can be parameterized by forest type and bulk deposition of TIN. The equations were obtained from 77 monthly measured deposition values of the different N species and the coefficient of determination was 0.92. We performed a limited test whether the approach can be transferred to other deposition and meteorological regimes based on the deposition data reported by Thimonier et al. (2019), which resulted in an underestimation of about 1 kg N ha^{-1} a^{-1}. However, the test is only valid to a limited extent. Data used for model parameterization and evaluation come from different years but partly from the same sites. Furthermore, only bulk deposition was measured at these sites, so the average conversion factors for Germany to estimate WD (Gauger et al., 2008) had to be used. Therefore, we can only assume that a rough estimate of gaseous HNO_3 and particular NO_3^- and NH_4^+ deposition is possible with this approach.

The EBM approach contains uncertainties at very different methodological and spatial levels. Comparison of spatial data in a 1*1 km grid resolution as for the EBM with point data as for the CBM and IFM should be done very carefully, especially in areas with complex orography or in regions with a fine-grained land cover pattern (edge effects) and with a high variability of N emissions. Actual deposition rates at a specific location may differ from the average of the corresponding EBM grid cell, although EBM output is reported on a land cover specific level (conifer, broadleaved and mixed forest). Similar to the other two approaches, EBM is affected by the uncertainties in wet deposition assessments. More importantly, as precipitation is highly variable in space and time, further uncertainty originates from the regionalization of precipitation, depending on regionalization strategy, orographic conditions and scale.

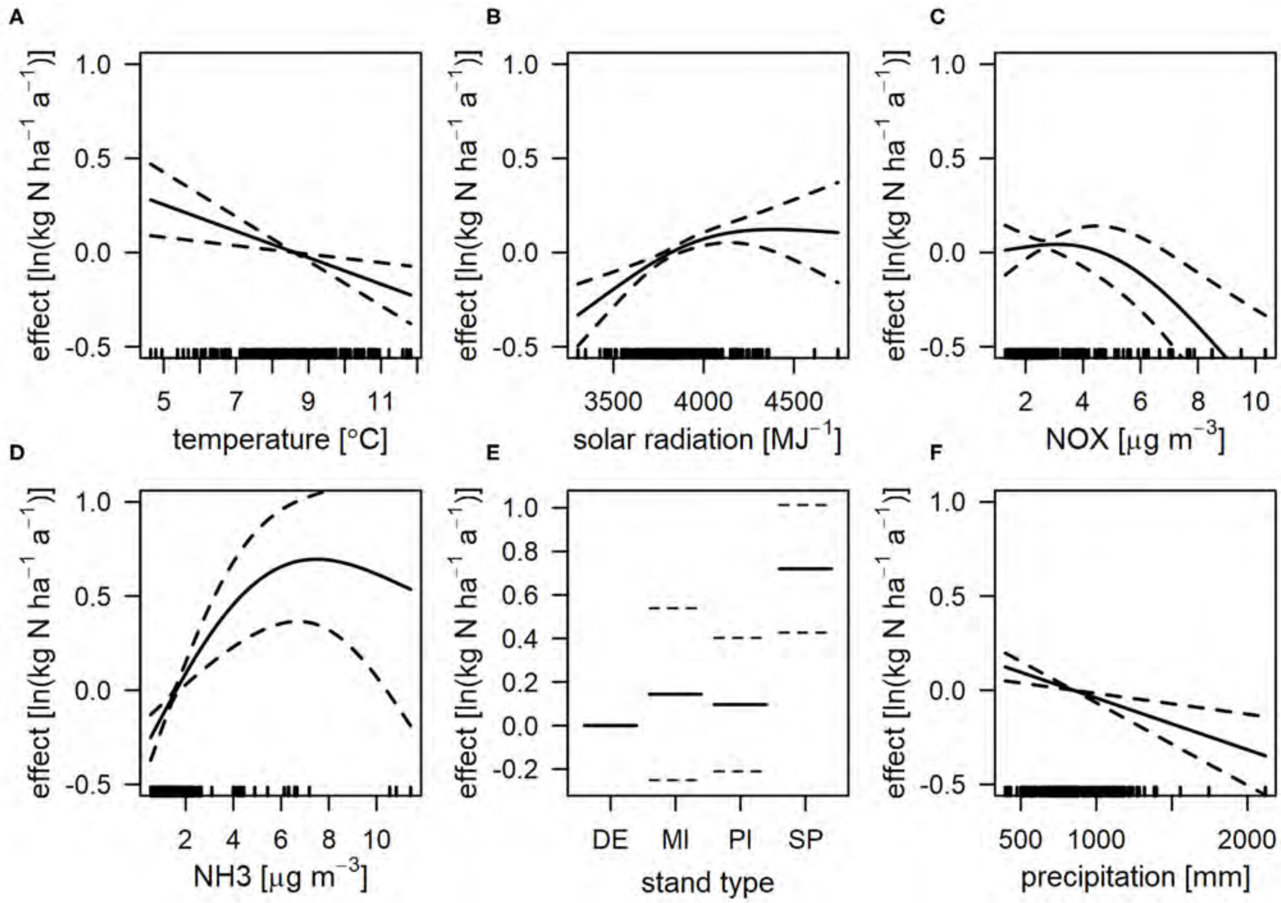

FIGURE 7 | Partial effect of temperature **(A)**, solar radiation **(B)**, NO_X concentration **(C)**, NH_3 concentration **(D)**, stand type **(E)**, and precipitation **(F)** on ΔTIN between the inferential (IFM) and emission based method (EBM) for dry deposition **(A–E)**, and total deposition **(F)**. Positive effects indicate a tendency for higher TIN deposition estimates of the IFM compared to the EBM. Note the log-transformed data. Dashed lines indicate 95% pointwise prognosis intervals. The covariate is displayed as marks along the x-axis. (DE, deciduous forest; MI, mixed forest; PI, pine forest; SP, spruce forest).

Considering these challenges to correctly estimate TIN WD, the average deviation of -0.8 kg N ha^{-1} a^{-1} compared to wet-only-corrected bulk deposition measurements for 1,237 plot-years in Germany is remarkably low. For dry deposition estimation Saylor et al. (2019) pointed out that the algorithms used in atmospheric chemistry models to predict particle deposition velocity are highly uncertain. In particular, estimates for forests show a weak agreement with available measurements (Saylor et al., 2019). Furthermore, the performance of EBM depends on the spatial resolution and quality of their input data, in particular the emission inventory. Meteorological data are available in a high temporal, but low spatial resolution of 7 × 14 km (Schaap et al., 2018). Accordingly, Simpson et al. (2011) estimated an error of TIN deposition estimates of 30% for the different regional models and approaches in Europe. A conceptual problem faced by all types of models is that relations established at specific locations are extrapolated to other areas (e.g., assumption of the CBM, dry deposition velocities, scavenging ratios, fog water enrichment factors) and proper parametrization of the transfer of these relations to other locations is challenging.

Comparison of TIN Deposition Estimates Between the Three Methods

We found on average a difference of -0.3 kg ha^{-1} a^{-1} and $+3.3$ kg ha^{-1} a^{-1} between the CBM and IFM approaches, with and without applying the extended semi-empirical deposition velocity correction factors given by Kirchner et al. (2014), respectively. The correction improves the fit between CBM and IFM across Germany (lowlands and mountain ranges), although it has been developed for the Bavarian Alps. Schmitt et al. (2005) found slightly higher estimates of the IFM (median difference $+2.4$ kg N ha^{-1} a^{-1}) when compared to a different CBM (De Vries et al., 2001), which, however, usually yields higher estimates of TIN deposition, compared to the Ulrich (1994) model used in our study (Mohr et al., 2005). Zimmermann et al. (2006) found a good agreement between the two methods, while Kirchner et al. (2014) stated that the two methods deviated at all sites. A slightly lower TIN deposition estimated by the CBM compared to the IFM may be expected due to the conceptual underestimation of TIN deposition by the specific type of CBM we used (Ulrich, 1994). However, the regression functions from Schmitt et al.

(2005) used in the IFM approach for estimating HNO_3, NH_4^+, and NO_3^- deposition may also lead to additional uncertainty of the deposition rates.

The statistical analysis of the differences in estimated TIN deposition between the IFM and CBM approaches found no significant effects of tree species, measurement year, coordinates, altitude, slope, aspect, aspect index, terrain exposure index (TEI), wind speed, air concentrations or precipitation. A large effect of the random factor "site" in the mixed model might indicate that further site-specific properties exists which contribute to the observed differences between model estimates in addition to random errors. Stand height, canopy closure, frontal area index (total area of roughness elements projected in the wind direction per unit ground area), crown density, and/or stand volume could be some of these site specific factors affecting local deposition processes (Erisman and Draaijers, 2003; Vesala et al., 2005; De Schrijver et al., 2007; Nakai et al., 2008).

A few studies exist where CBM and/or IFM have been compared to micro-meteorological measurements of higher accuracy. Recently, Brümmer et al. (2020) have tested an eddy covariance approach for total reactive nitrogen in a forested area of the Bavarian forest with low levels of N deposition. For the period 2016–2018 they report a measured TIN DD rate of around 4.4 kg ha^{-1} a^{-1} compared to estimates of 5.2 and 6.9 kg ha^{-1} a^{-1} from the same EBM as used in our study (based on an uncorrected and an improved classification of land use types, respectively). In parallel, a CBM approach is conducted at the site since several years (Beudert and Breit, 2014). However, the CBM results are not comparable with our study, because the variants of the CBMs they use clearly differ from the Ulrich (1994) model used in our study. Mohr et al. (2005) found clearly lower N fluxes (−27 kg N ha^{-1} a^{-1}) with the CBM compared to a micrometeorological method at a site exposed to high ambient air levels of NH_3.

The comparison of WD using the EBM approach with the CBM shows a fairly good agreement. However, there seems to be a systematic deviation for estimates with increasing precipitation rates (**Figure 5A**). This effect mainly originates from two mountainous stations. At these stations, the simulated precipitation amount clearly exceeds the open field precipitation observations. If the corresponding stations are excluded from the statistical analysis, the effect is still significant, but the effect strength is somewhat smaller (results not shown). The deviation in the precipitation data might be caused by a systematic underestimation of precipitation amount for observations with a large proportion of snow or strong rain events (sampler overflow) and/or low performance of regionalization models for precipitation in orographic complex landscapes as used for WD estimation (1*1 km). The elevated deviance between EBM and CBM estimates in some regions might be attributable to the uniform application of bulk to wet conversion factors (**Figure 6A**).

The EBM approach estimates on average lower DD compared to CBM and IFM approaches (**Table 6**). This pattern is more distinct for spruce plots (**Figure 5F**, **Figure 7E**) and does not diminish if the tree-species correction factor of the IFM approach is deactivated (**Table 7**, model "IFM_{VT}-EBM"). As the CBM and the IFM rely on independent approaches to estimate the dry deposition, this might indicate that the EBM deposition estimates are less reliable for spruce plots. When interpreting the partial effects, however, the relationship between individual variables must always be taken into account. Accordingly, the change in nitrogen deposition should not be deduced directly from the tree species spruce, for example, but rather the respective precipitation conditions (and other variables) at the site must also be considered. Several meteorological parameters significantly affect the differences between DD estimates, which are also known to have an effect on deposition rates [e.g., via stomatal resistance, particle deposition velocity; Han et al. (2011), Mohan (2016)]. On the other hand, the different terrain parameters hardly contribute to an explanation. This may be due to incorporation of terrain information into the regionalization of the climatic variables that were used as predictors (Dietrich et al., 2019).

In a previous comparison between the EBM used in our study and the CBM according to De Vries et al. (2001), TIN TD estimates were reported to roughly agree (Schaap et al., 2018). At some locations, however, differences of up to 40% were found (Schaap et al., 2018). Our analysis is, however, not directly comparable to the Schaap et al. (2018) study, as (1) a different type of CBM was used; (2) a larger number of plots with an extended regional coverage of Germany and longer observation periods are included; (3) a bulk-to-wet correction of NH_4^+, NO_3^-, and Na^+ fluxes has been applied prior to CBM calculations as recommended by Adriaenssens et al. (2013) in order to harmonize the WD calculation between the three approaches. This correction increases the estimated TIN TD of the CBM by ~1.2 kg ha^{-1} a^{-1} on average.

CONCLUSIONS AND OUTLOOK

The demand for N deposition estimates with high accuracy as well as large spatial and temporal resolution is growing. Forests pose a special challenge in this regard, due to the high importance of dry deposition, which is more difficult to quantify. In the framework of long-term monitoring at ICP Forests sites in Germany, we compared three methods for the estimation of total inorganic nitrogen deposition to forests (CBM, IFM, EBM). If all approaches would yield accurate results, we would have expected similar TIN deposition estimates from the IFM and the EBM and lower values from the CBM, as it includes a conceptual underestimation. Contrarily, we found the EBM provided on average lowest estimates. The deviation between the EBM and both of the other methods was especially pronounced for the dry deposition at spruce plots. Differences of dry deposition estimates between all methods were found to be affected by meteorological conditions, which are known to regulate deposition velocity. The average discrepancy in TIN deposition according to the method yielding on average highest deposition rates (IFM) and the method suggesting on average lowest deposition rates (EBM) was 6.3 kg N ha^{-1} a^{-1} (uncorrected IFM) or 2.7 kg N ha^{-1} a^{-1} (IFM with site specific corrections). We hypothesize that a combination of different factors contribute to the discrepancies between the three approaches. They include the comparison of observations at the plot scale (CBM, IFM) with gridded information (EBM, based on a 1 × 1 km resolution and coarser for some calculation steps), conceptual limitations of the utilized CBM version, and varying accuracy of the EBM for different forest types.

As all methods are subject to considerable uncertainty, we cannot conclude whether any of the methods provides more or less accurate estimates. Instead, the results can only indicate aspects worthwhile to consider for future methodological improvements. Recent developments contributing to a more accurate quantification of TIN deposition to forests include for example (i) continuous improvements of EBM and the underlying emission inventories (Schaap et al., 2015, 2017, 2018), (ii) networks of low-cost monitoring stations for ambient air concentrations and meteorological conditions improving data availability (e.g., Karagulian et al., 2019; Weissert et al., 2020), and (iii) ongoing research in CBM and similar approaches, like surface-wash and surrogate surface sampling (Aguillaume et al., 2017; Karlsson et al., 2019). In addition, more high-accuracy validation datasets (e.g., Brümmer et al., 2020) are required to quantify the performance of the different modeling approaches.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request from the institutions holding the data: Climate and terrain data by Institute of Geography, University of Hamburg, Germany. Emission based deposition data by UBA, Dessau, Germany. Measured deposition and air concentrations by Thünen Institute of Forest Ecosystems, Eberswalde, Germany. Deposition calculated by inferential methods by Northwest German Forest Research Institute (NW-FVA). Requests to access these datasets should be directed to Jan Wehberg, jan.wehberg@uni-hamburg.de; Markus Geupel, markus.geupel@uba.de; Anne-Kartin Prescher, anne.prescher@thuenen.de; Bernd Ahrends, bernd.ahrends@nw-fva.de.

AUTHOR CONTRIBUTIONS

BA and AS: designed the study, developing of methods, preparation of deposition data, and data analysis. JW: regionalization of climate data and realization of terrain analysis. A-KP: preprocessing and aggregation of air concentration data. MG: emission based deposition data. HA and HM: supervising the work. All authors contributed to writing.

FUNDING

The evaluation was based on data that was collected by partners of the official UNECE ICP Forests Network (http://icp-forests.net/contributors). Part of the data was co-financed by the European Commission. Partial funding of data collection was provided by the European Union under Council Regulation (EEC) 3528/86 on the Protection of Forests against Atmospheric Pollution, the Regulation (EC) 2152/2003 concerning monitoring of forests and environmental interactions in the community (Forest Focus) and by the project LIFE 07 ENV/D/000218 Further Development and Implementation of an EU-level Forest monitoring Systeme (FutMon).

ACKNOWLEDGMENTS

We thank the numerous staff involved in operating the intensive forest monitoring in Germany in the last decades. We thank the German Environmental Agency for providing the data from EBM approach. However, it should be noted that this paper does not necessarily reflect the opinion or the policies of the German Federal Environment Agency.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/ffgc.2020.00103/full#supplementary-material

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

4. Underestimation of potassium in forest dry deposition? – A simulation experiment in rural Germany

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Underestimation of potassium in forest dry deposition? A simulation experiment in rural Germany

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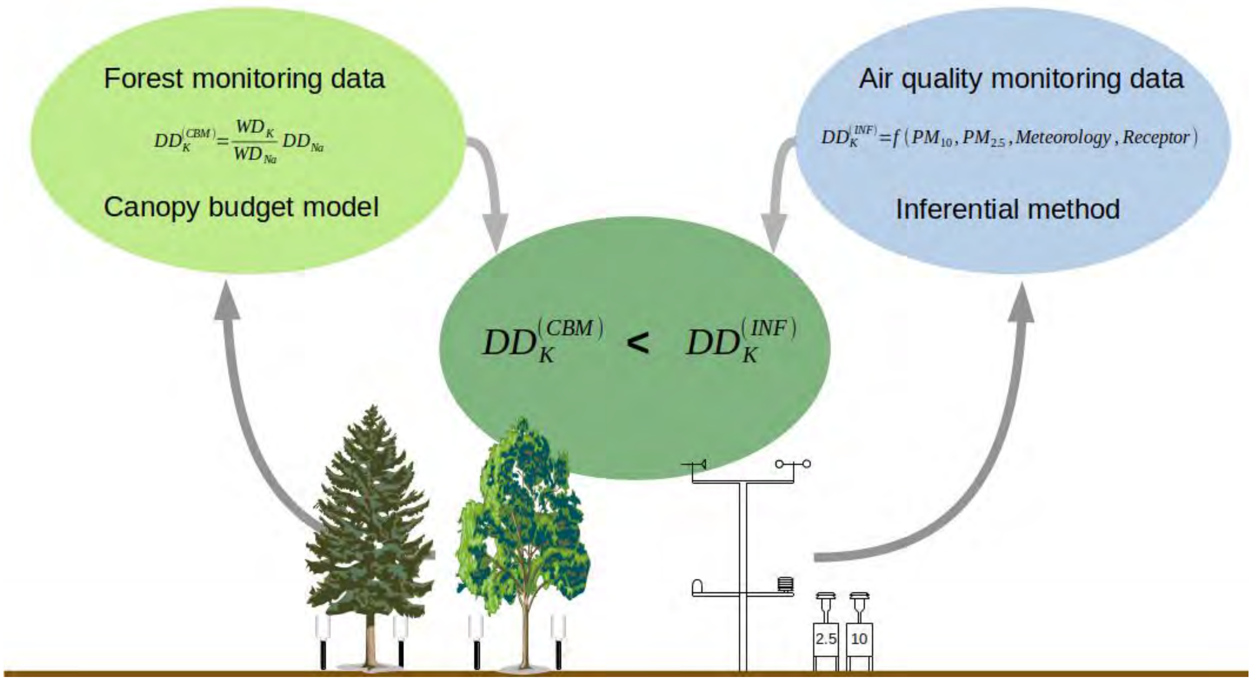
Abstract

Measurements of throughfall (TF) and wet deposition (WD) are a common method to assess base cation deposition to forests. If information on TF and WD is available, dry deposition (DD) is typically calculated with a canopy budget model (CBM) assuming similar base cation to Na^+ ratios in WD and DD. This assumption is especially uncertain for K^+ ions, since they are often bound to smaller particles compared to Na^+ ions. We assess this assumption by comparing the DD of K^+ estimated with the CBM (DD_K^{CBM}) to the DD of K^+ simulated with a process-oriented DD model ("inferential model", DD_K^{IFM}). Simulation experiments were performed at two indicator forest stands ("virtual" broadleaved (BL) and coniferous (CF) forest) at a rural monitoring site ("Melpitz") in Germany based on daily $PM_{2.5}$ and PM_{10} concentrations and weekly WD observations. On average, the K^+:Na^+ ratio in WD was 0.24 but the K^+:Na^+ ratio in DD^{IFM} was 0.43 (CF) and 0.4 (BL). Accordingly, DD_K^{CBM} would need to be multiplied by a correction factor of 1.77 (CF) and 1.66 (BL) to match DD_K^{IFM}. Uncertainty arises from periods affected by presence of particles larger than 10 µm diameter, not covered by local measurements. A corresponding lower boundary estimate for the average underestimation of DD_K^{CBM} is a correction factor of 1.37 (CF) and 1.29 (BL). Furthermore, structural uncertainty is originating from the choice of the IFM model variant. We therefore consider our results as a potential indication but not as evidence of an underestimation of DD_K by the CBM approach.

Graphical abstract



Introduction

Information on atmospheric deposition to forests is essential for monitoring the success of clean air policy and a prerequisite for addressing many questions in forest ecology. For example, trends and effects of the deposition of eutrophying and acidifying substances are regularly assessed in the context of pollution reduction efforts (Ferretti et al., 2020; Forsius et al., 2021) and knowledge about the atmospheric deposition of nutrients is crucial for applying a sustainable forest management that avoids nutrient depletion of forest sites (Ahrends et al., 2022; Vanguelova et al., 2022). However, the reliable quantification of atmospheric total deposition to forests remains challenging because the forest canopy is a large receptor for dry and occult deposition (together denoted as DD), which are difficult to measure. Costly and labour-intensive methods to directly assess DD can provide reliable measurements but have only been applied at a restricted number of sites and during limited measurement campaigns (Brümmer et al., 2022; Emerson et al., 2020; Hansen et al., 2015; Ruijgrok et al., 1997). Data with a larger spatial and temporal coverage originates from measurements of throughfall, stemflow, and open field deposition. For example, currently around 300 monitoring stations provide such information within the pan-European forest monitoring network “ICP Forests” (Marchetto et al., 2021). Calculating atmospheric deposition from these measurements is, however, complicated by the simultaneous occurrence of canopy exchange and DD and the need to disentangle atmospheric inputs from the circulation of substances between soil and trees (Parker, 1983).

A common tool for deriving information on DD from measurements of throughfall, stemflow, and open field deposition are so-called “canopy budget models” (CBMs; De Vries et al., 2001; Draaijers and Erisman, 1995; Ulrich, 1994). In this group of calculation schemes, one of the measured substances is assumed to be neither taken up nor being leached from the forest canopy (“tracer substance”) (Bredemeier, 1988). With this property, the DD of the tracer substance can be calculated as the difference between the substance flux under the forest canopy (throughfall + stemflow) and wet deposition (WD) measured outside the forest. The approach is extended by assumptions on concentration ratios in DD (relative to the tracer) and assumptions on canopy exchange processes (van der Maas and Pape, 1991). In this way, CBMs are conceptually able to distinguish between canopy exchange and DD, yielding estimates of the atmospheric deposition of nitrogen, sulphur and base cations. CBMs are widely used in scientific studies in many regions (Ahrends et al., 2020; Brumme et al., 2021; Matsumoto et al., 2020; Staelens et al., 2008; Van Langenhove et al., 2020). The various assumptions in the different calculation steps introduce, however, considerable uncertainty in the resulting estimates. For example, Adriaenssens et al. (2013) reported that the estimated total N deposition ranged between 10 and 25 kg N ha^{-1} a^{-1}, depending on the chosen CBM variant. This uncertainty complicates the application of CBMs at wider spatial scales and in the context of assessing the performance of clean air policy (Thimonier et al., 2019).

One of the uncertainties in CBM calculations arises from the assumption about ratios in DD compared to WD. Specifically, most studies applying CBM approaches rely on sodium ions (Na^+) as tracer substance and assume that the ratio of base cations (BC) to Na^+ (K^+:Na^+, Ca^{2+}:Na^+, Mg^{2+}:Na^+) is similar in DD and WD:

$$\frac{DD_{BC}}{DD_{Na}} = \frac{WD_{BC}}{WD_{Na}} \qquad (1)$$

This allows calculating the DD for each of the three BC (DD_K, DD_{Ca}, DD_{Mg}):

$$DD_{BC} = DD_{Na} \frac{WD_{BC}}{WD_{Na}} \tag{2}$$

Estimates of DD_{BC} based on this assumption have been applied in a several of contexts, e.g. in assessments of nitrogen saturation and soil acidification (Brumme et al., 2021; Meesenburg et al., 2016; Talkner et al., 2010) or for evaluating the sustainability of forest management scenarios (Ahrends et al., 2022). Furthermore, knowledge on DD_{BC} is required for calculation N uptake via ion exchange in some CBM variants (De Vries et al., 2001; Draaijers and Erisman, 1995).

The CBM assumption (eq. 1) is based on the assumption of similar sizes of BC-containing particles (Draaijers and Erisman, 1995; Thimonier et al., 2005) and thus similar behaviour in terms of DD and WD (in-cloud and below-cloud scavenging of particles). For forest stands where occult deposition accounts for a large proportion of DD, the approach has also been motivated by the assumption of similar substance ratios in fog droplets compared to rain drops (Ulrich, 1994). Occasionally, it has been questioned for a variety of reasons (Staelens et al., 2008). In particular, the assumption of similar particle sizes for K^+ and Na^+ has been mentioned as a potential source of bias. For example, Adriaenssens (2012) corrected the K^+:Na^+ ratios in WD by a factor of 0.32 when applying the CBM to account for K^+ being bound to smaller particles compared to Na^+. The prevalence of smaller particle sizes of K^+ compared to Na^+ is supported by emission inventories. For example, Hellsten (2007) report a PM_{coarse}:PM_{fine} ratio of 0.22 for K^+ and 0.7 for Na^+ in Europe-wide BC emissions. Draaijers et al. (1997) report a mass median diameter of 2.5 µm for K^+ compared to 5.1 µm for Na^+ at a forest stand in the Netherlands. In contrast to the hypothesis that differences in particle size should translate into a bias in CBM-based estimates, they found good agreement between estimates of DD_K from the CBM compared to results from an inferential particle DD model (IFM) over a study period of six month. On the other hand, Adriaenssens et al.

(2013) suggest that information on differences in BC particle sizes should be used to update the CBM where possible.

In this study, we address the question to what extent the CBM assumption holds when using the K^+ and Na^+ measurements made at the rural background research station Melpitz (Germany). We used six years of daily BC aerosol concentration measurements and an IFM (Emerson et al., 2020) to calculate DD to two indicator forest stands ("virtual" broadleaf and conifer forest with tree heights typical for monitoring sites in that region). We compare the K^+:Na^+ ratios in $DD^{(IFM)}$ to the K^+:Na^+ ratios that would result from the CBM at that site and quantify the differences in DD_K estimates between the two methods. We check the plausibility of the IFM by comparing $DD_{Na}^{(IFM)}$ rates to observations from ICP Forests Intensive Monitoring ("Level II") stations in the same region and investigate the robustness of our approach with a sensitivity analysis.

Methods

Study site

DD modelling and comparison of K^+:Na^+ ratios between DD and WD is conducted based on the measurements made at the research station Melpitz, Germany (51.52°N, 12.93°E, 86 m a.s.l.), which provides long-term time series of the required model input parameters. The site is located approximately 40 km north east from the city of Leipzig. It is operated by the Leibniz Institute for Tropospheric Research (TROPOS) and is part of the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP, station code DE0044R), the Global Atmosphere Watch (GAW) and European Aerosol, Clouds and Trace Gases Research Infrastrucure (ACTRIS). The site is located on a mown grassland of approximately 400 m x 500 m size, surrounded by agricultural land (Spindler et al., 2001). The main wind direction is south-west with marine and continental air masses that have crossed large parts of western Europe and the city of Leipzig. A second important wind direction is east with anthropogenically affected air masses from Poland, Belarus, Ukraine, Slovakia and the Czech Republic (Spindler et al., 2012). More information on the site and the existing measurement program can be found in several publications (Aas et al., 2012; Alastuey et al., 2016; Spindler et al., 2012, 2010, 2004, 2001; Stieger et al., 2018). In order to check the plausibility of the modelled DD rates, we also included data from those five ICP Forests Level II stations closest to the Melpitz site (see section “Plausibility check” and Fig. 1).

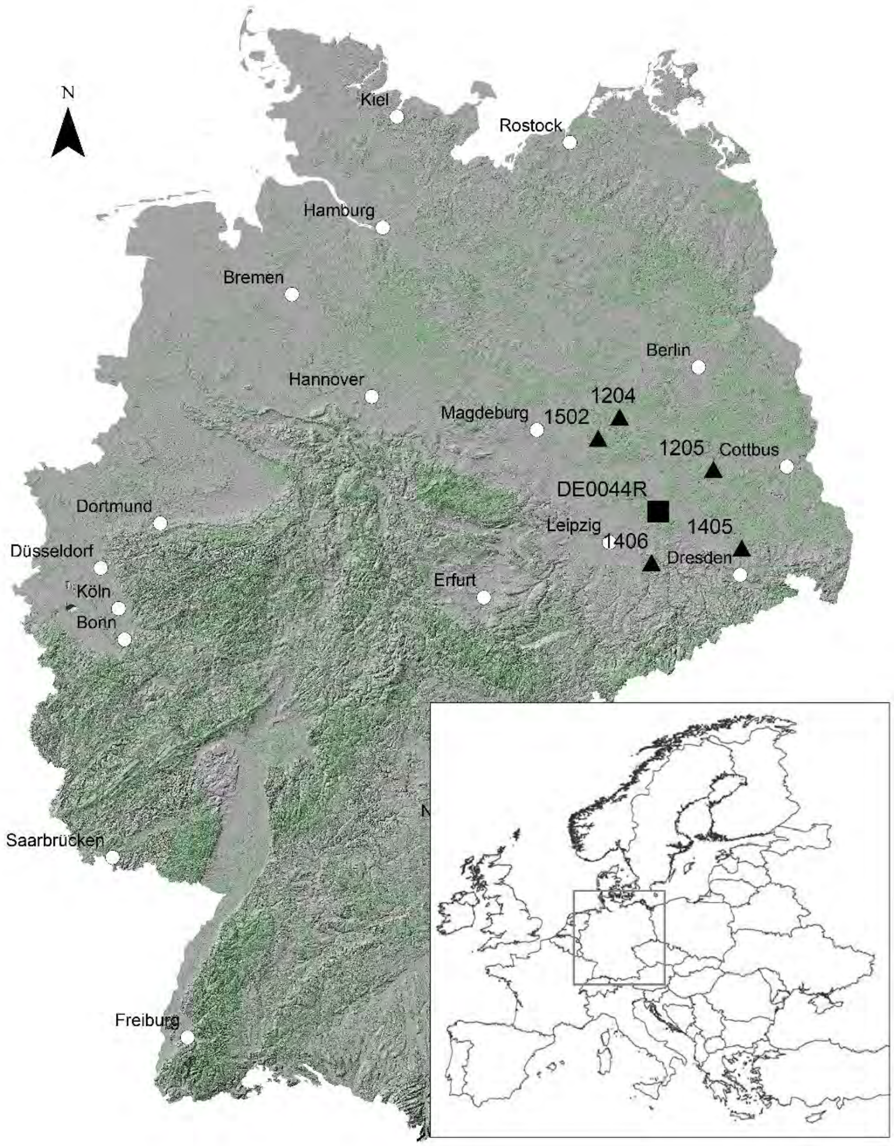


Fig. 1 EMEP measurement site Melpitz (DE0044R) and the five ICP Forests intensive monitoring sites in the same region. Produced using Copernicus WorldDEM™-90 © DLR e.V. 2010-2014 and © Airbus Defence and Space GmbH 2014-2018 provided under COPERNICUS by the European Union and ESA

Precipitation and aerosol data

Daily particulate matter ($PM_{2.5}$ and PM_{10}) BC concentrations as well as weekly wet-only precipitation volume and concentrations from the Melpitz site from the beginning of measurements to 2021 were downloaded from the EBAS database (ebas.nilu.no, Tørseth et al., 2012, accessed in April 2021). Data were obtained for the two substances of primary interest (K^+ and Na^+). In addition, data for Mg^{2+} and Ca^{2+} were downloaded, which were only used in the data preparation step to support identification of periods with potential contamination by soil particles (see section “Air concentrations” below). Annual data summaries from the PM and WD observations at Melpitz are regularly published in the EMEP data reports (e.g. Hjellbrekke, 2014). The sampling and analytical methods follow the EMEP manual for sampling and chemical analysis (EMEP/CCC, 2014). All available data was filtered and gap-filled according to the steps described below. After this process, six years of $PM_{2.5}$, PM_{10} and WD data for both substances (K^+ and Na^+) remained (2004, 2005, 2006, 2008, 2010 and 2013). An overview of abbreviations used in this paper is provided in table 1.

Table 1: Overview of abbreviations

Term	Meaning
Fine particles ($PM_{2.5}$)	Particles with an aerodynamic diameter ≤ 2.5 µm
PM_{10}	Particles with an aerodynamic diameter ≤ 10 µm
Coarse particles (PM_{coarse})	Particles with an aerodynamic diameter > 2.5 µm and ≤ 10 µm
Giant particles	Particles with an aerodynamic diameter > 10 µm
v_d	Dry deposition velocity (cm s^{-1})
z_M	Height of air concentration measurements (1.5 m)
z_b	Blending height (50 m)
z_0	Roughness length (land-use dependent, see text)
d	Displacement height (land-use dependent, see text)
CBM	Canopy budget model
IFM	Inferential model
WD	Wet deposition (kg ha^{-1} a^{-1})
DD	Dry deposition of aerosols to land surface (in this study also including occult (fog) deposition) (kg ha^{-1} a^{-1})
DD^{IFM}	DD calculated according to the inferential approach, i.e. calculated as the product of air concentration and dry deposition velocity (kg ha^{-1} a^{-1})
DD^{CBM}	DD calculated according to the CBM, i.e. calculated from measurements of throughfall and wet deposition (kg ha^{-1} a^{-1})
ω	Scavenging ratio (definition according to eq. 3)

Air concentrations

PM sampling is conducted at 1.5 m above ground using high volume samplers Digitel DHA-80 (Digitel Elektronik AG, Hegnau, Switzerland) (Spindler et al., 2004). Particles with an upper diameter of 10 µm (PM_{10}) and 2.5 µm ($PM_{2.5}$) are both sampled on preheated quartz fiber filter (105°C) (Muntkell, type MK360, Sweden) for 24h from midnight to midnight. Before and after sampling, the filters were conditioned for 48h at 22°C and 50% RH before being weighted. For water soluble ions, the filters were extracted in ultrapure water (> 18 MΩ/cm) and analysed by Ion Chromatography (ICS-3000 Dionex). Further information on sample preparation and analysis can be found in Spindler et al. (2012). Daily PM concentrations from the EBAS database were filtered for data flags (https://projects.nilu.no//ccc/flags/). Values flagged as “unspecified error” or “dust contamination” were removed. A small proportion of daily concentration measurements (maximum proportion per year: 13%) were below the detection limit of 15 ng m^{-3} (Spindler et al. 2010). Since the objective of this study is to compare deposition rates at the annual level and because days with such low concentrations contribute only marginally to the total annual fluxes, we included values in this concentration range (i.e. below 15 ng m^{-3}) without changes. We kept only years for which $PM_{2.5}$ and PM_{10} measurements of both substances were available for at least 90% of the year at this stage of data preparation. In order to account for diurnal patterns in meteorological variables, DD modelling is conducted on an hourly basis (see below). Thus, it was necessary to convert the daily concentrations to hourly data. We assigned the daily average concentration to each hour of the respective daily measurement interval. For example, at a daily average concentration of 0.25 µg m^{-3}, we assume the concentration in each hour was 0.25 µg m^{-3}. An analysis showing that this downsampling approach has only little effect on the long-term (e.g. annual) deposition sums is provided in Online Resource S4 section “Sensitivity check for the temporal resolution of air concentrations”. A similar approach based on daily average concentrations has for example also been used to simulate base cations dry deposition at the

Speulder forest in the Netherlands (Erisman and Draaijers, 1995). At this stage, 26 calendar days did not have full coverage due to measurement gaps or data deleted during data cleaning steps described above. We filled each missing hour by the average concentration over a time period including the past 15 days and future 15 days. Online Resource S1 shows the time series of concentrations after data cleaning and gap filling.

Our approach relies on the assumption that particles larger than 10 µm diameter ("giant particles") do not contribute significantly to total air concentrations for Na^+ and K^+, such that PM_{10} and $PM_{2.5}$ measurements yield a relatively complete picture of the Na^+ and K^+ aerosol load in the air. We assume this holds for Na^+, because potential sources of Na^+ containing giant particles are largely absent: (a) The distance from the coast is approx. 400 km and giant particles typically deposit very fast, (b) street deicing in winter is probably not relevant at the rural Melpitz site (Spindler et al., 2010) and (c) Na^+ concentrations in soil are relatively low (Hoogerbrugge et al., 2012). With regards to K^+, however, previous studies at the Melpitz site mention occasional re-suspension of material from dry surfaces surrounding the measurement station, e.g. due to wind blow and agricultural activities including fertiliser application (Spindler et al., 2010; Stieger et al., 2018). In contrast to emissions from combustion processes, a relevant share of soil dust particles is in the giant particle range (Lazaridis et al., 2001). We therefore excluded periods where measured K^+ concentrations likely do not reflect total K^+ concentrations in the air, due to the presence of giant particles. These periods can be characterised by unusually high WD concentrations in relation to measured PM_{10} concentrations, because giant particles are easily captured by raindrops (Wang et al., 2010) and are thus included in WD measurements, but missing in PM_{10} measurements. The ratio of WD concentrations to measured air concentrations is expressed by the scavenging ratio (ω, corrected for the density of air (1.2 kg m^{-3} (Legg, 2017)) and water (Cheng and Zhang, 2017):

$$\omega = \frac{c_{precip}}{c_{air}} \frac{\rho_{air}}{\rho_{water}} \tag{3}$$

We used ω as a metric to identify giant particle episodes. The approach is conducted in three steps: (1) Calculation of the scavenging ratio of K^+ (ω_K), (2) identification of a threshold level (ω^*) above which relevant contribution from giant particles is suspected, and (3) exclusion of periods where ω_K exceeds ω^*. The approach is described in detail in Online Resource S2. In summary, 7 months (≈10%) of data were excluded. All excluded months are within the period from May to October and elevated ω_K often coincides with elevated ω_{Ca} and partly also ω_{Mg}, suggesting a common origin, i.e. likely particles from soil dust. For the entire study, these periods were excluded for all calculations (WD, air concentrations and DD). The exception is the plausibility check (see below), where gapless data from the six years is used for the comparison to ICP Forests Level II monitoring stations (Na^+ only, therefore not affected by giant particles).

Wet deposition

Weekly precipitation volumes and concentrations were available from measurements with a WADOS wet-only sampler (http://www.kroneis.at/umweltanalyse/1-wados). We applied the following data cleaning steps in the given order. First, we split those sampling periods that overlapped New Year's Day into two periods, such that each period is fully included in one year. We distributed the precipitation amount proportional to the duration of the sampling period in the new / old year. Data below the detection limit were treated as half of the detection limit, which was the case for 3.5% of the data. Missing concentrations were set to zero in case of low precipitation (below 5 mm per week). This included all concentrations flagged as "Low precipitation, concentration unknown" (flag 783). The data were filtered for those years with air concentrations available (see above). The resulting temporal coverage per substance and year was at least 98%.

Weekly deposition rates were then calculated as the product of concentration and precipitation volume. Deposition rates and precipitation volume were summed up per year. The remaining small data gaps (< 2% of the year) were filled by assuming annual average deposition rates in the time periods with data gaps. Volume weighted annual mean concentrations were calculated by dividing the annual deposition rates by the annual precipitation volume. WD time series are shown in Online Resource S3.

Meteorological data

The IFM (see below) operates with hourly meteorological data. In order to ensure gapless and consistent meteorological data, we used data from the ERA5 dataset family provided by the European Centre for Medium-Range Weather Forecasts (ECMWF) via the Copernicus Climate Change Service Data Store. The following parameters have been downloaded from the dataset "ERA5-Land hourly data from 1950 to present" (9 km grid) (Muñoz-Sabater et al., 2021): "10m u component of wind", "10m v component of wind", "2m dew point temperature", "2m temperature", "surface pressure", "surface solar radiation downwards". The parameter "total cloud cover" was only available from the dataset "reanalysis-era5-single-levels" on coarser resolution (0.25° x 0.25°) (Hersbach et al., 2018). Horizontal wind speed was calculated from u- and v-components of wind. Relative humidity was calculated from temperature and dew point using the August-Roche-Magnus equation (Alduchov and Eskridge, 1997). We assessed the effects of potential bias in meteorological parameters in the sensitivity analyses (see below).

Dry deposition modelling

We employed the common "inferential approach" for DD modelling (Wesely and Hicks, 2000). In this approach, the particle dry deposition flux F (=DD^{IFM}) is the product of a DD velocity v_d and the corresponding concentration (c) at height z:

$$F \; = \; v_d(z)\, c(z) \qquad (4)$$

We applied the resistance analogy approach (see below), in order to account for important determinants of v_d, such as wind speed, particle size and receptor properties (roughness length, surface wetness, etc.). In order to use the measured air concentrations (1.5 m height over grassland) for the calculation of the DD to the two indicator forest stands, we applied the so-called blending height concept. The blending height (z_b) is the height at which "concentrations and meteorological parameters are not influenced by surface properties to a large extent" (Erisman and Draaijers, 1995). The blending height approach is for example used by the ECMWF ERA5 model to calculate wind speed at 10 m over a hypothetical open-terrain grassland surface (ECMWF, 2016). For the application of the blending height concept to our setup, we proceed as follows (see Fig. 2). In a first step, we calculate F at the (grassland) measurement site (M) using locally measured concentrations and v_d modelled for the measurement height (z_M = 1.5 m).

$$F^{(M)} \; = v_d^{(M)}(z_M)\, c^{(M)}(z_M) \qquad (5)$$

Based on the common assumption that F does not change with height within the surface layer of the atmosphere ("constant flux layer", Seinfeld and Pandis (2006)) a second equation for $F^{(M)}$ can be constructed based on the v_d and concentration at z_b:

$$F^{(M)} = v_d^{(M)}(z_b)\, c(z_b) \tag{6}$$

The concentration at blending height ($c(z_b)$) is by definition independent of the underlying land use. By rearranging these equations, $c(z_b)$ can be calculated from measured air concentrations and modelled v_d as:

$$c(z_b) = \frac{v_d^{(M)}(z_M)}{v_d^{(M)}(z_b)}\, c^{(M)}(z_M) \tag{7}$$

The DD flux to the indicator broadleaf (BL) or conifer (CF) forest is then calculated as:

$$F^{(BL)} = v_d^{(BL)}(z_b)\, c(z_b) \tag{8}$$

$$F^{(CF)} = v_d^{(CF)}(z_b)\, c(z_b) \tag{9}$$

A similar procedure is for example used in chemical transport models to calculate land-type specific surface air concentrations from concentrations in higher model layers for diagnostic purposes (i.e. for comparison with measured air concentrations) (Simpson et al., 2012).

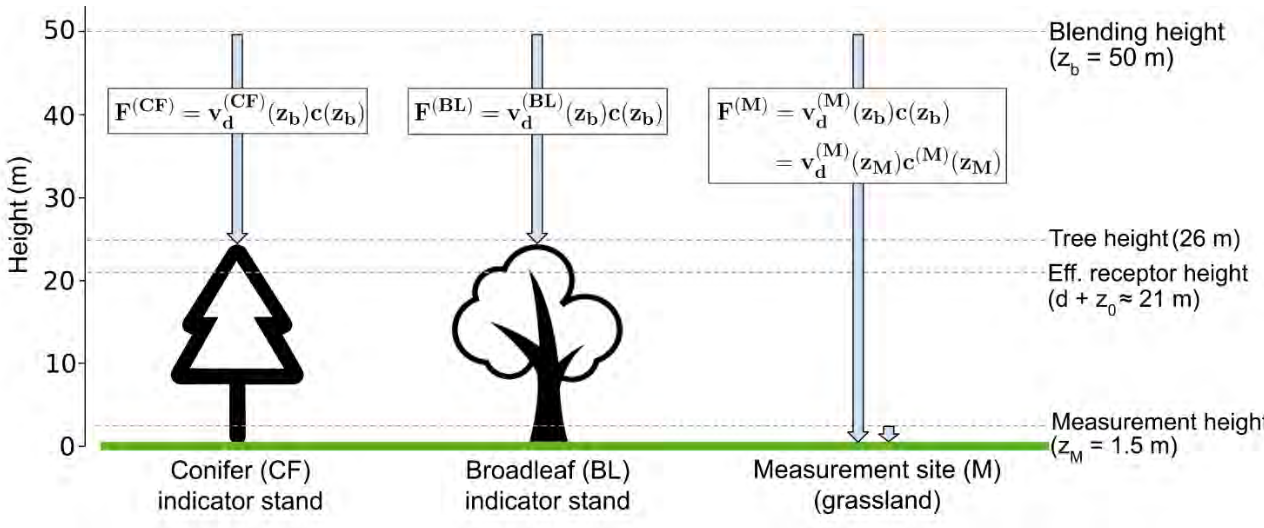


Fig. 2 Dry deposition modelling setup. The deposition flux to the grassland measurement site ($F^{(M)}$) can be calculated based on air concentration (c) and deposition velocities (v_d) at measurement height or at blending height. This allows for calculating the air concentration at blending height from air concentrations at measurement height and modelled v_d at the two heights (see eq. 7). In the next step, the deposition flux to the broadleaf $F^{(BL)}$ and conifer $F^{(CF)}$ indicator stands is calculated based on air concentrations at blending height and modelled v_d. See text for details

In order to calculate the v_d for different heights and receptors (grassland measurement site, CF, BL), we employ the widely used resistance analogy for DD modelling (Seinfeld and Pandis, 2006). Specifically, we use the common particle DD model of Zhang et al. (2001) with the recent update by Emerson et al. (2020) to calculate v_d. In this approach, the v_d for a specific particle is the sum of a gravitational settling velocity v_g and the inverse of the sum of two resistances (aerodynamic resistance R_a and surface resistance R_s).

$$v_d = v_g + \frac{1}{R_a + R_s} \tag{10}$$

R_s and v_g depend on particle size. We distribute the measured PM_{10} and $PM_{2.5}$ concentrations into six particle size bins (representing particles with diameters between 0.05 µm and 10 µm) according to results from an impactor study conducted at the measurement site (Spindler et al., 2012). Calculation of DD fluxes is performed separately for each size bin. A detailed description of the particle size distribution, the DD calculation procedures and the verification of the model implementation are provided in Online Resource S4. In summary, we proceeded as follows for the calculation of annual DD fluxes with the IFM:

1. Calculate PM_{coarse} from daily PM_{10} and $PM_{2.5}$ (=PM_{fine}) concentrations for each substance.
2. Assign the daily concentration to each hour of the respective daily measurement period, perform gap-filling where necessary.
3. Distribute hourly PM_{coarse} and PM_{fine} among the size bins (see Online Resource S4).
4. Calculate 24 v_d values for each hour: Six particle sizes and four combinations of height and receptor (grassland measurement site at 1.5 m measurement height, grassland measurement site at 50 m blending height, each of the two indicator forest stands at 50 m blending height).
5. Calculate the concentration of each substance in each size bin at the blending height using the constant flux assumption.
6. Calculate the hourly DD flux to BL and CF by multiplying the respective air concentration at blending height with the respective v_d. This results in 24 hourly fluxes (two substances, two forest receptors, six size bins).
7. Aggregate the fluxes over size bins and over hours per year, resulting in four annual dry deposition rates (two substances and two forest receptors).

A summary of parameters used for DD modelling is given in table S4.6. All calculations have been conducted with the R programming language (R Core Team, 2020). The DD modelling code is available as an R package (https://github.com/AndSchmitz/ddpart).

Quantification of deviation from the CBM

The CBM assumes equal K^+:Na^+ ratios in WD and DD (eq. 1). The aim of this study is to test this assumption. This is done with the IFM described above. In order to quantify deviations from the CBM, we add a “correction factor” (f_{corr}) to the CBM-based expression for DD_K from eq. 2:

$$DD_K = f_{corr} \, DD_{Na} \frac{WD_K}{WD_{Na}} \qquad (11)$$

If both DD and WD rates are known (from measurements or detailed modelling), f_{corr} can be calculated as:

$$f_{corr} = \frac{DD_K}{DD_{Na}} \frac{WD_{Na}}{WD_K} \qquad (12)$$

In our case, we used measured WD rates and DD rates from the IFM to calculate f_{corr}. The original CBM assumes a f_{corr} = 1. The sign and magnitude of f_{corr} quantify by which factor CBM-based estimates of DD_K would need to be corrected in order to match the modelled DD_K. I.e. f_{corr} > 1 indicates underestimation and f_{corr} < 1 indicates overestimation of the CBM compared to the IFM.

Plausibility and robustness checks

The correction factor for the CBM compared to the IFM (f_{corr}) depends only on the ratio and not on the absolute magnitude of $DD_{Na}^{(IFM)}$ and $DD_{K}^{(IFM)}$ (eq. 12). Nevertheless, we check whether the absolute magnitude of DD^{IFM} rates is within a plausible range (plausibility check). The plausibility check is conducted by comparing $DD_{Na}^{(IFM)}$ modelled at the Melpitz station to DD rates observed at ICP Forests Level II sites. In order to have roughly similar conditions in terms of Na^+ air concentrations and particle size (distance to coast), we selected the five ICP Forests plots closest to the Melpitz station (distances to Melpitz between 38 km and 79 km). Deposition data was derived from the national ICP Forests Level II database (see section Data Availability Statement). All plots are stocked by Scots pine (*Pinus sylvestris*) with the exception of plot 1406 which is stocked by sessile oak (*Quercus petraea*). Each station provides deposition data from an open field site and from within the forest stand (throughfall), based on permanently open ("bulk") samplers. Stemflow is typically only considered relevant at beech plots (Clarke et al., 2022) and therefore assumed to be negligible at the five plots used for the plausibility check. Information on sample collection, storage and analyses is provided in Ahrends et al. (2020). Annual WD_{Na} is calculated from bulk open field deposition based on a bulk to wet-only conversion factor of 0.81 established by Gauger et al. (2008) as an average over Germany. Annual DD_{Na} is calculated as the difference of annual throughfall and annual WD_{Na}, assuming that Na^+ is neither taken up nor leached from the forest canopy ("tracer property", see Introduction). The plausibility check is limited to Na^+, because only the DD of Na^+ and not the DD of K^+ can be calculated directly from forest monitoring data (DD = throughfall + stemflow - WD) without relying on the CBM (see Introduction).

In a second step, we check that the K^+:Na^+ ratios in modelled DD (and therefore also f_{corr}) are robust against uncertainty in the DD model inputs. This robustness check is conducted as a local sensitivity analysis (Morio, 2011) of K^+:Na^+ ratios in modelled DD to variation in the DD model input (receptor properties and meteorological variables). We changed one parameter at a time, keeping all other parameters constant, and compared the results to the "baseline parametrization" (i.e. parametrization as described above). The main parameters were increased and decreased by 30% compared to the baseline parametrization in order to demonstrate the sensitivity of model results to parametrization errors.

Results

Air concentrations

Fig. 3 shows the annual average concentrations of K^+ and Na^+ in PM_{10} and the respective contributions of PM_{fine} and PM_{coarse}. The PM_{10} concentration is higher for Na^+ (average of approx. 0.26 µg m^{-3}) compared to K^+ (average of approx. 0.18 µg m^{-3}). The Coarse:Fine ratio is approximately 2:1 for Na^+ while it is approximately 1:3 for K^+. Both coarse and fine concentrations of K^+ are lower in 2013 compared to the other years (see Discussion).

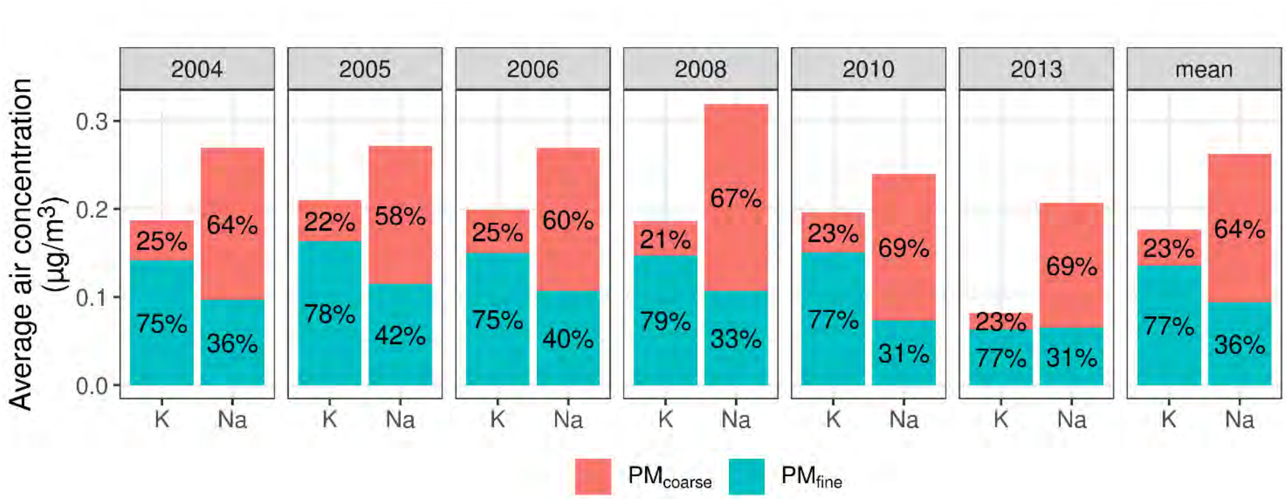


Fig. 3 Annual average PM_{10} concentrations per substance (K^+, Na^+) and shares of PM_{coarse} and PM_{fine} among PM_{10}. The last panel shows the average over the six-year study period

Dry deposition velocities and deposition rates

Table 2 summarises the DD modelling results over the study period, roughly following the order of calculations steps. In the following text, results are described only for Na^+ (numbers for K^+ in table 2). The average deposition flux to the grassland measurement site amounts to 0.18 mg m^{-2} d^{-1}, resulting from a modelled effective mean v_d at measurement height (z_M = 1.5 m) of 0.77

cm s^{-1} and measured air concentrations of 0.26 µg m^{-3}. The modelled effective mean v_d at blending height (z_b = 50 m) is lower (0.27 cm s^{-1}) due to the larger aerodynamic resistance (R_a), caused by the greater difference in height. The calculated air concentration at z_b is 0.76 µg m^{-3}, resulting from the deposition flux to the grassland measurement site and the effective mean v_d at z_b to the grassland measurement site (eq. 7). This concentration is higher compared to the concentration measured at z_M, reflecting the vertical concentration gradient from the particle source (atmosphere) to the particle sink (ground). Air concentrations at z_b are by definition independent of the underlying land use and therefore have identical values for all three receptors. The modelled effective mean v_d at z_b to the two indicator forest stands is 0.61 cm s^{-1} (BL) and 1.33 cm s^{-1} (CF), exceeding the modelled effective mean v_d at z_b to the grassland measurement site due to the larger surface area and larger effective receptor height of forest ($d+z_0 \approx 21$ m). The deposition flux to BL and CF resulting from air concentration and the effective mean v_d at z_b is 0.40 mg m^{-2} d^{-1} and 0.88 mg m^{-2} d^{-1}, respectively.

Table 2: Average PM_{10} concentration (c in µg m^{-3}), effective dry deposition velocities (v_d in cm s^{-1}) and DD flux (F in mg m^{-2} d^{-1}) over the entire study period

Receptor	**RefHeight**	**K^+**			**Na^+**		
		c	v_d	F	c	v_d	F
Grassland	z_M	0.177	0.429	0.066	0.263	0.771	0.175
	z_b	0.663	0.114	0.066	0.764	0.265	0.175
ForestBL	z_b	0.663	0.282	0.162	0.764	0.612	0.404
ForestCF	z_b	0.663	0.651	0.373	0.764	1.326	0.875

Fig. 4 shows the average deposition rates per substance and receptor (CF, BL). In line with higher air concentrations of Na^+ compared to K^+, also DD and WD of Na^+ exceed the corresponding rates for K^+. The average annual WD of Na^+ is 1.04 kg ha^{-1} a^{-1} while it is 0.25 kg ha^{-1} a^{-1} for K^+. DD to CF is on average 2.89 kg ha^{-1} a^{-1} for Na^+ compared to 1.23 kg ha^{-1} a^{-1} for K^+. DD to BL is on average 1.33 kg ha^{-1} a^{-1} for Na^+ compared to 0.53 kg ha^{-1} a^{-1} for K^+. The CF:BL ratio based on average annual DD rates is 2.2 for Na^+ and 2.3 for K^+. Note that "annual deposition" does not refer to complete years because two months in 2008 and one month in all other years have been excluded from calculations due to the presence of giant particles (see Methods).

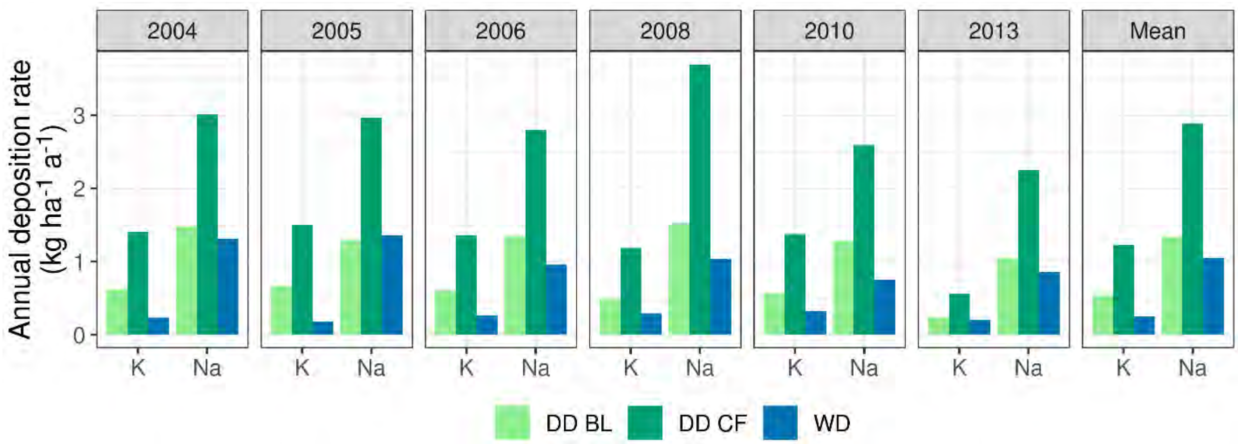


Fig. 4 Measured wet deposition (WD) rates and modelled dry deposition (DD^{IFM}) rates to the two indicator forest stands (broadleaf: BL, conifer: CF). Note that comparability between years is limited because periods affected by giant particles (>10 μm diameter) have been excluded (see Methods)

K^+:Na^+ ratios in deposition and air concentrations

K^+:Na^+ ratios in annual WD and DD as well as in annual averages of PM_{10} are shown in Fig. 5. On average, the K^+:Na^+ ratio is 0.24 in WD, 0.67 in PM_{10}, 0.43 in DD to the CF indicator stand and 0.4 in DD to the BL indicator stand. K^+:Na^+ ratios show considerable variation between years. For example, in measured WD the lowest value is 0.13 (2005) and the highest value is 0.43 (2010). For DD, the values range between 0.23 (DD BL 2013) and 0.53 (DD CF 2010) with little difference between CF and BL. K^+:Na^+ ratios in PM_{10} (PM_{fine} + PM_{coarse}) are generally higher than K^+:Na^+ ratios in WD and DD.

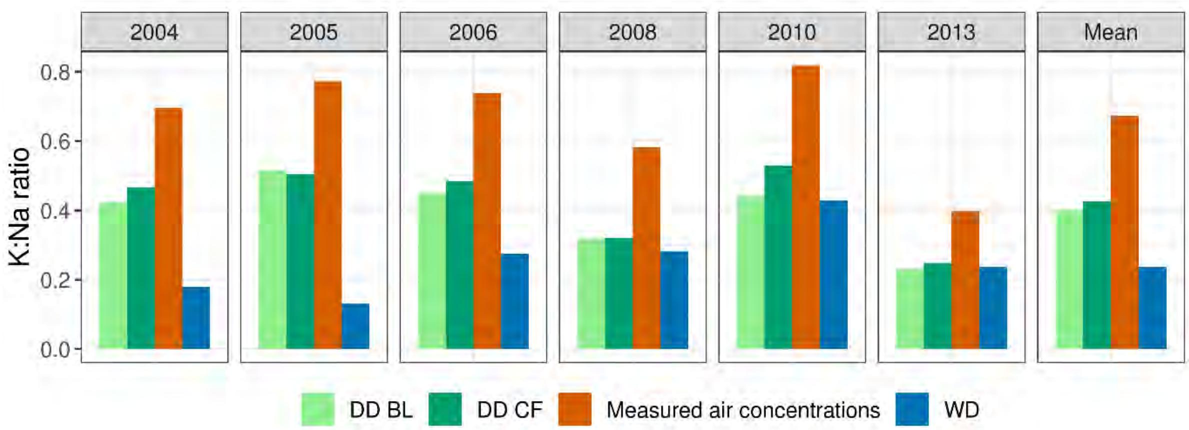


Fig. 5 K^+:Na^+ ratios in measured wet deposition (WD), air concentrations (PM_{10}) and modelled dry deposition ($DD^{(IFM)}$) for the two indicator forest stands (broadleaf: BL, conifer: CF). According to the CBM, K^+:Na^+ ratios in WD and DD are identical. Note that comparability between years is limited because periods affected by giant particles (>10 µm diameter) have been excluded (see Methods)

Deviations between DD estimates from the CBM and the IFM

Table 3 lists the DD rates from the IFM ($DD^{(IFM)}$) and observed WD rates, as well as DD_K calculated according to the CBM ($DD_K^{(CBM)}$). The deviations between $DD_K^{(CBM)}$ and $DD_K^{(IFM)}$ are quantified by f_{corr}, which is calculated such that $DD_K^{(CBM)}\ f_{corr} = \ DD^{(IFM)}$ (see Methods). The IFM estimates an average annual K^+ deposition rate to the BL indicator stand of 0.53 kg ha^{-1} a^{-1} compared to 0.32 kg ha^{-1} a^{-1} resulting from the CBM. This corresponds to a 66% higher DD_K according to the IFM compared to the CBM, indicated by f_{corr} = 1.66. f_{corr} is slightly higher for CF in most years and also on average (1.77). Across all years, f_{corr} ranges between 0.98 (BL in 2013) to 3.89 (BL in 2005). As an additional perspective on the robustness, f_{corr} has also been calculated for the grassland (GR) measurement site (although CBM-based DD estimates are in practice only applied for forests). Despite the differences in receptor properties, f_{corr} for GR is typically in a similar range compared to BL and CF.

Table 3: Annual and time-average modelled dry deposition rates according to the IFM ($DD^{(IFM)}$) and observed wet (WD) deposition rates of K^+ and Na^+ to conifer (CF) and broadleaf (BL) indicator stands. "f_{corr}" indicates the factor by which the CBM based estimates of K^+ dry deposition ($DD_K^{(CBM)}$) would need to be multiplied in order to match the corresponding rate of $DD_K^{(IFM)}$. As an additional perspective on the robustness of f_{corr}, results are also provided for the grassland (GR) measurement site, although the CBM approach is usually only applied to forests

Year	WD_{Na}	WD_K	$DD_{Na,CF}^{(IFM)}$	$DD_{Na,BL}^{(IFM)}$	$DD_{Na,GR}^{(IFM)}$	$DD_{K,CF}^{(IFM)}$	$DD_{K,BL}^{(IFM)}$	$DD_{K,GR}^{(IFM)}$	$DD_{K,CF}^{(CBM)}$	$DD_{K,BL}^{(CBM)}$	$DD_{K,GR}^{(CBM)}$	$f_{corr,CF}$	$f_{corr,BL}$	$f_{corr,GR}$
2004	1.31	0.23	3.01	1.48	0.61	1.41	0.63	0.25	0.53	0.26	0.11	2.67	2.42	2.33
2005	1.36	0.18	2.97	1.3	0.58	1.5	0.67	0.26	0.39	0.17	0.08	3.82	3.89	3.39
2006	0.96	0.26	2.8	1.34	0.56	1.36	0.6	0.24	0.76	0.36	0.15	1.79	1.65	1.58
2008	1.04	0.29	3.69	1.53	0.71	1.18	0.49	0.21	1.03	0.43	0.2	1.15	1.15	1.06
2010	0.75	0.32	2.59	1.29	0.54	1.37	0.57	0.24	1.11	0.55	0.23	1.24	1.04	1.04
2013	0.86	0.2	2.25	1.05	0.46	0.56	0.24	0.1	0.52	0.24	0.11	1.07	0.98	0.93
Mean	1.04	0.25	2.89	1.33	0.58	1.23	0.53	0.22	0.69	0.32	0.14	1.77	1.66	1.58

Plausibility and robustness checks

Plausibility check

Fig. 6 shows the comparison of Na^+ deposition rates at the Melpitz indicator forest stands with ICP Forests Level II plots in the same region. DD_{Na} rates at the ICP Forests plots span one order of magnitude (0.31 kg ha^{-1} a^{-1} at plot 1205 in 2010 to 5.2 kg ha^{-1} a^{-1} at plot 1502 in 2005). The modelled DD_{Na} to the CF indicator forest at the Melpitz station is in upper part of this range (average: 3.1 kg ha^{-1} a^{-1}), ranked second or first in individual years among all CF stands. Modelled and observed DD_{Na} to BL stands is lower compared to CF stands. The modelled DD_{Na} to the BL indicator stand is on average higher (1.5 kg ha^{-1} a^{-1}) compared to the broadleaf (oak) ICP Forests plot 1406 (0.9 kg ha^{-1} a^{-1}). WD_{Na} rates at the ICP Forests plots range between 1.3 kg ha^{-1} a^{-1} (plot 1405 in 2010) and 3.0 kg ha^{-1} a^{-1} (plot 1204 in 2013). The average WD_{Na} measured at the Melpitz site is lower than this range (1.1 kg ha^{-1} a^{-1}) and WD_{Na} at Melpitz is also the lowest WD_{Na} in each individual year. Note that throughout this study annual WD_{Na} and DD_{Na} rates are calculated excluding one or two months per year where giant particles of K^+ have been identified (see Methods), but Na^+ data in this section refers to complete years to allow for comparison with data from ICP Forest plots.

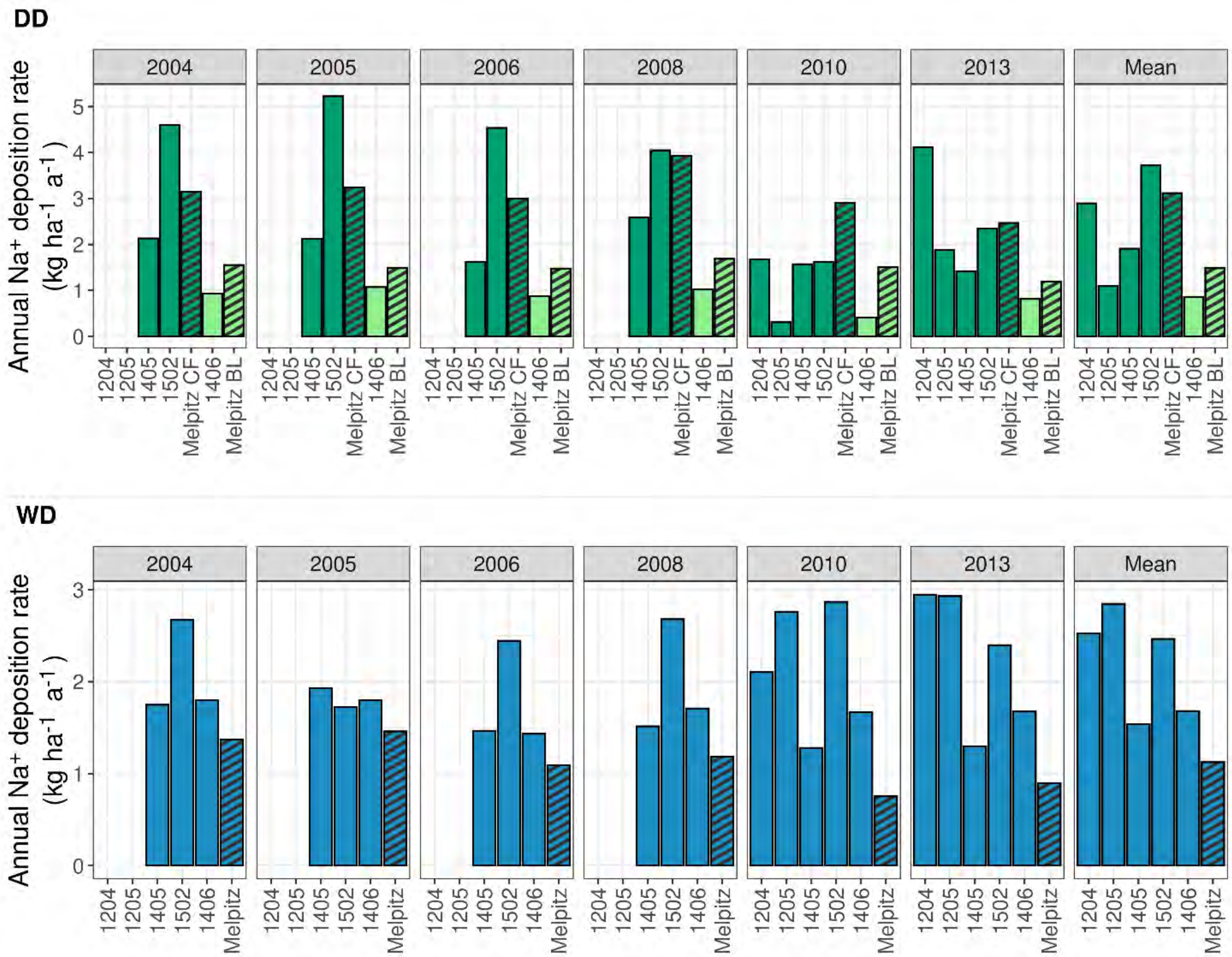


Fig. 6 Comparison of dry (DD) and wet (WD) rates of Na^{+} at the measurement site Melpitz (hatched, indicator CF and BL forest) and ICP Forests Level II plots in the same region (pine: 1204, 1205, 1405, 1502; oak: 1406). Light green represents BL, dark green represents CF. Missing bars indicate no data available for the respective plot-year

Robustness check

The robustness check indicated a relatively high sensitivity of absolute annual DD rates to changes in wind speed and to a lesser extent also to roughness length, displacement height and blending height. For example, a 30% increase in wind speed increased the DD of Na^+ to the CF indicator stand by 29%. Using a blending height of 100 m instead of 50 m reduced DD to the CF indicator stand by 12%. In contrast, K^+:Na^+ ratios were very robust against changes in the parametrization. The largest overall effect was a 1% decrease of the K^+:Na^+ ratio in DD to the CF indicator stand, resulting from a 30% decrease of wind speed (Fig. 7).

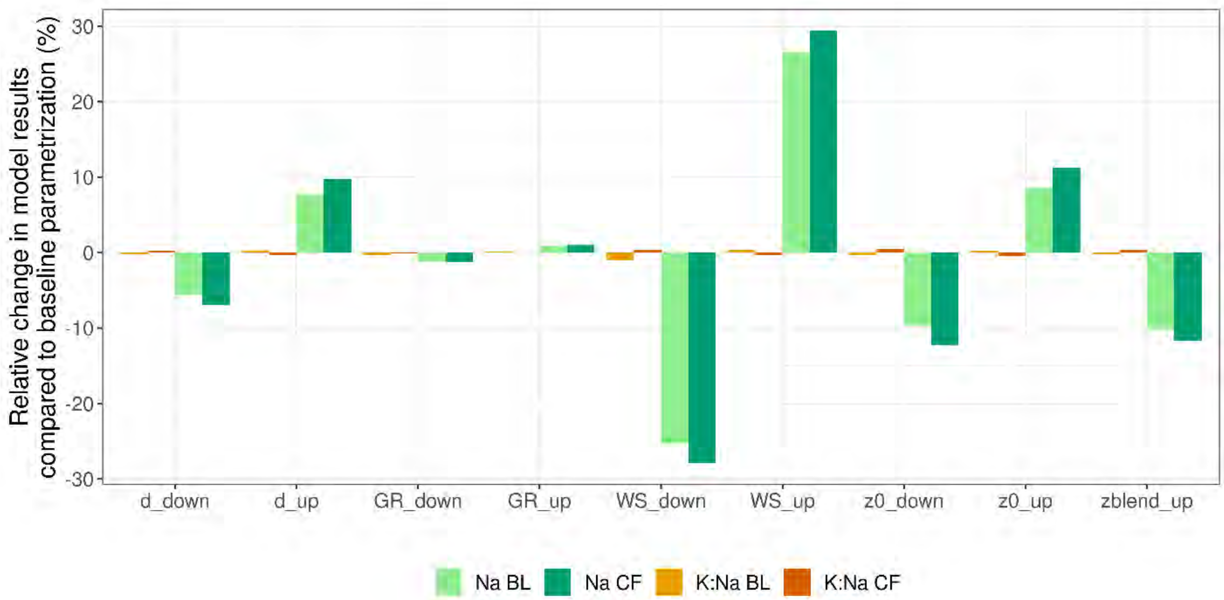


Fig. 7 Results of the robustness check (sensitivity analyses) of the process-oriented dry deposition model (IFM) parametrization. The height of the bars indicates the percentage deviation of the response variables from the values observed under the baseline parametrization, averaged over the six-year study period. The response variables are the DD of Na^+ to the broadleaf (Na^+ BL) and conifer (Na^+ CF) indicator stands and the K^+:Na^+ ratios in DD to the two indicator stands (K^+:Na^+ BL, K^+:Na^+ CF). The parameter variations considered are a 30% decrease („down“) and 30% increase („up“) in the displacement height (d), the global radiation (GR), the wind speed (WS), the roughness length (z_0). For blending height, the default value (50 m) was changed to 100 m, as both values are occasionally used (von Salzen et al., 1996). The parameter values used in the baseline parametrization are listed in table S4.6

Discussion

Dry deposition modelling

This study is based on the IFM suggested by Emerson et al. (2020), which updates the commonly used model by Zhang et al. (2001). The update aims to better match v_d measurement data that has become available in the 20 years between the two publications. Our implementation of the model has been verified by reproducing the relation between v_d and particle size as shown in Fig. 1 and 2 in Emerson et al. (2020) (see Online Resource S4). Aerodynamic resistance calculations have been checked against Spindler et al. (2001), who modelled the DD flux of NH_3 to the Melpitz site for a 17-day period in September 1995. They report the sum of aerodynamic resistance and quasi-laminar resistance (mostly dominated by aerodynamic resistance (R_a)) between 1 m measurement height and the grassland receptor surface (Fig. 5 in Spindler et al. (2001)). The values range between 0 s m^{-1} and 100 s m^{-1} with occasional peaks of greater atmospheric stability where R_a reaches around 500 s m^{-1}. For our study period, we find that R_a between 1.5 m measurement height and the grassland receptor has a 5% quantile of 21 s m^{-1}, a median of 49 s m^{-1} and a 95% quantile of 151 s m^{-1}. Considering the difference in time periods, we conclude that the calculation approach for R_a chosen in our study yields results in the same range as Spindler et al. (2001) derived from micrometeorological in-situ measurements. Hofschreuder et al. (1997) reported v_d values for K^+ and Na^+ calculated from concentrations recorded at 29 m height and DD fluxes measured with a number of different techniques over a forest stand stocked by Douglas fir (22 m tree top height) in the Netherlands. Their v_d values range between 1.6 cm s^{-1} to 3.5 cm s^{-1} for K^+ and between 0.8 to 5.0 cm s^{-1} for Na^+, depending on the DD flux measurement method (excluding branch washing where leaching of K^+ could not be ruled out). These results are somewhat higher compared to v_d values at the conifer indicator stand in our study (v_d at 50 m height of 0.68 cm s^{-1} for K^+ and 1.21 cm s^{-1} for Na^+). These differences might be expected, as Hofschreuder et al. (1997) consider their reported v_d to be "high" due to a large leaf are index (one-sided LAI between 9 and 10 according to Erisman et al. (1997)) and large share of PM_{coarse} among aerosols in their study (e.g. at least 56% of K^+ in PM_{coarse} according to table 2 in Hofschreuder et al. (1997)). The plausibility check (Fig. 6) showed that $DD_{Na}^{(IFM)}$ modelled at the Melpitz site is roughly in the same range as observations at regional ICP Forests Level II sites, although with a tendency for higher DD rates (especially for BL). We conclude that the IFM yields roughly plausible results. As discussed below, our main results (f_{corr}, depending on ratios and not on absolute deposition rates) are relatively robust against changes in meteorology and receptor properties. We therefore do not expect our conclusions to change if the IFM would be fine-tuned to match the conditions at a specific forest stand in the vicinity of the Melpitz site.

K^+:Na^+ ratios and performance of the CBM

f_{corr} shows substantial variation between years. In the first two years of the study period (2004 and 2005), K^+:Na^+ ratios in WD are very low but K^+:Na^+ ratios in DD are relatively high (Fig. 5), yielding very high values of f_{corr} (2.42 - 3.89). In 2006, Na^+ WD drops from 1.31 kg ha^{-1} a^{-1} (2004) and 1.36 kg ha^{-1} a^{-1} (2005) to 0.96 kg ha^{-1} a^{-1}, potentially linked to variation in weather patterns (lower transport of sea salt from the coast). Correspondingly, K^+:Na^+ in WD is higher than in previous years. Interestingly, this drop in Na^+ WD is not associated with corresponding changes in Na^+ air concentrations (Fig. 3) and therefore K^+:Na^+ ratio in DD is similar to the two years before. This higher K^+:Na^+ ratio in WD at relatively constant K^+:Na^+ ratio in DD lead to a lower f_{corr} (BL: 1.65, CF: 1.79) compared to previous years (Fig. 5). In 2008, Na^+ PM_{coarse} concentrations increase (Fig. 3), which reduces K^+:Na^+ ratios in DD compared to previous years (Fig. 5). This leads to very similar K^+:Na^+ ratios in WD and DD (f_{corr} = 1.15 for both CF and BL). In 2010, K^+:Na^+ ratios in both WD and DD rise by a similar amount compared to 2008 (Fig. 5). This is related to a reduction in

Na^+ WD and Na^+ in air concentrations (and associated DD). The resulting f_{corr} is 1.04 for BL and 1.24 for CF. Finally, in 2013, K^+ air concentrations drop to around 50% of all previous years (Fig. 3), with an associated drop in K^+:Na^+ ratios in DD. K^+ in WD also drops in 2013 compared to the previous three years. This leads to balanced K^+:Na^+ ratios between WD and DD with f_{corr} values of 0.98 (BL) and 1.07 (CF). In summary, $DD_K^{(CBM)}$ matches $DD_K^{(IFM)}$ reasonably well in last three years of the study period (2008, 2010 and 2013; f_{corr} between 0.98 and 1.24). In the first three years, however, $DD_K^{(CBM)}$ would need to be corrected by a factor of 1.65 to 3.89 to match $DD_K^{(IFM)}$. Temporal variation of f_{corr} between years seems to be often driven by somewhat independent variation of Na^+ air concentrations and Na^+ WD.

In general, K^+:Na^+ ratios are smaller in both DD and WD compared to PM_{10} (Fig. 5). This is expected because both DD and particle scavenging by precipitation are less effective for smaller particles (down to a certain diameter below which efficiencies rise again). This implies that substance ratios in both DD and WD are shifted towards substances bound to larger particles, relative to substance ratios in the air. If this size-dependence of aerosol filtering by precipitation and vegetation was perfectly symmetric and no other aspects would be involved, the CBM would generally hold, also in case of size differences between BC and Na^+. However, there is no theoretical reason to assume this symmetry and competing models describing these relations substantially disagree (Emerson et al., 2020; Saylor et al., 2019; Wang et al., 2010). In addition, WD is also affected by air masses in higher altitudes that are not necessarily completely mixed with ground level air. This means that the chemical and physical composition of air filtered by vegetation (ground level) can differ from the composition of the air column traversed by precipitation (both in-cloud and below-cloud scavenging) (Matsumoto et al., 2020). We observed that temporal variation in WD_{Na} is not always matched by corresponding changes in ground level Na^+ air concentrations, potentially hinting to decoupled rainout vs. washout contributions. A more extreme case of K^+:Na^+ ratios is reported by Ferm and Hultberg (1999). They provide 5-year average deposition ratios between non-marine K^+ (K_{nm}^+) and Na^+ in WD and on a Teflon string sampler (as a surrogate surface for conifer needles). The molar $K_{nm}^+ : Na^+$ ratio is 0.008 for the Teflon string compared to 0.07 for WD. Converting molar to mass-based substance ratios and applying eq. 12, the f_{corr} for their setting is 0.11. This means that, in contrast to our study, CBM-based calculations would need to be reduced by a factor of 0.11 to match DD_K estimates based on DD ratios from the Teflon sampler. These results might be explained by the fact that their measurement site is located only 15 km away from the open Swedish west coast (Ferm and Hultberg, 1999) with corresponding high rates of Na^+ WD. This supports earlier suggestions that the CBM should not be applied close to the coast (Ulrich, 1994), due to incomplete vertical mixing of the air with associated differences between rainout and washout.

Besides surrogate surface sampling, also other approaches have been used to correct for suspected shortcomings of the CBM. For example, Adriaenssens (2012) used a correction factor of 0.32 when applying the CBM to estimate DD_K at an individual beech tree in the Belgium, based on substance-specific v_d values. This approach accounts only for the size-specific shift in substance ratios between air concentrations and DD. It implicitly assumes that substance ratios in WD are a good proxy for substance ratios in the air. By contrast, in our study both processes were important: (1) The shift in substance ratios between WD and air concentrations and (2) the shift in substance ratios between air concentrations and DD. Matsumoto et al. (2020) observed substantial differences between $NO_3^- : Na^+$ ratios in surface level air concentrations compared to $NO_3^- : Na^+$ratios in WD. To reduce bias in subsequent calculations of DD_{NO3} to a forest stand in Japan (extending the CBM to $NO_3^- : Na^+$), they used the air concentration ratios and not the WD concentration ratios for DD calculations. In contrast to our results, Draaijers et al. (1997) report a perfect fit between $DD_K^{(CBM)}$ and $DD_K^{(IFM)}$ based on around 6 month of micrometeorological measurements at a Douglas fir site in the Netherlands. In their study, also DD_{Na} matched well between the two approaches.

The IFM used in our study indicated on average 66% (BL) and 77% (CF) higher annual DD_K compared to CBM-based estimates. Despite these substantial relative differences, the absolute difference in DD_K is rather small, due to the generally low annual DD_K rates (0.53 kg ha^{-1} a^{-1} (IFM) vs. 0.32 kg ha^{-1} a^{-1} (CBM) for BL and 1.23 kg ha^{-1} a^{-1} (IFM) vs. to 0.69 kg ha^{-1} a^{-1} (CBM) for CF). These low absolute concentrations and deposition rates might also partly explain the large variability between years and high sensitivity to the giant particle data cleaning steps (see below), as for example small changes in WD can have large effects on f_{corr}. In addition to calculating DD_K, the CBM is often used to calculate of the sum of the base cation DD ($DD_{\Sigma\mathrm{BC}}^{(CBM)}$ = $DD_K^{(CBM)}$+ $DD_{Mg}^{(CBM)}$+ $DD_{Ca}^{(CBM)}$) and the total deposition of inorganic nitrogen ($TD_N^{(CBM)}$). The average annual $DD_{\Sigma\mathrm{BC}}^{(CBM)}$ at the five ICP Forests stands in the same region in the six-year study period ranges between 0.07 keq ha^{-1} a^{-1} (plot 1405) and 0.24 keq ha^{-1} a^{-1} (plot 1204). If $DD_K^{(CBM)}$at these sites is adjusted by the respective annual f_{corr} values found at Melpitz, average annual $DD_{\Sigma\mathrm{BC}}^{(CBM)}$ increases by between 1% (plot 1205) and 22% (plot 1406). This would translate into slightly higher estimates for the speed of recovery from soil acidification and suggest slightly better forest ecosystem nutrient balances. $DD_{\Sigma\mathrm{BC}}^{(CBM)}$ is also relevant for the calculation of nitrogen canopy update according to some canopy budget models (De Vries et al., 2001; Draaijers and Erisman, 1995). Adjusting $DD_K^{(CBM)}$ at the five ICP Forests stands by the respective annual f_{corr} values found at Melpitz reduces canopy uptake according to the model by De Vries et al. (2001) between 1% (plot 1205) and 9% (plot 1502). As the share of canopy uptake among total N deposition is relatively low at these plots (between 13% (plot 1405) and 21% (plot 1406)), the average $TD_N^{(CBM)}$ is reduced by less than 2% at all plots, when applying f_{corr}. These corrections are small compared to the generally large methodological uncertainties in the estimation of N deposition to forests (Ahrends et al., 2020; Braun et al., 2022).

Limitations of the approach

We chose the indicator forest stand approach (virtual forests, Schmidt-Walter et al. (2019), Thiele et al. (2017)) because no ICP Forests Level II station is directly co-located at the Melpitz site. Therefore, in absence of local measurements, DD_{Na} rates required for the CBM calculations had to be taken from the IFM (i.e. $DD_{Na}^{(\mathrm{IFM})}$ is used to calculate $DD_K^{(CBM)}$). This induces some level of circularity in our argumentation: We use results from the IFM on one hand to calculate the results according to the CBM and on the other hand to check the validity of the CBM (by comparing $DD_K^{(CBM)}$ to $DD_K^{(\mathrm{IFM})}$). We address this issue by showing that our results (f_{corr}) only marginally depend on the specific receptor properties. This means that any calibration efforts to make the $DD_{Na}^{(\mathrm{IFM})}$ match observed DD_{Na} rates at a specific forest stand in the vicinity of the Melpitz site would have little effect on our conclusions in terms of performance of the CBM. This is indicated by the fact that annual f_{corr} is similar for different receptors like broadleaf and conifer forest and even for grassland (table 3). Also, changes in wind speed and other meteorological conditions have only small effects on f_{corr} (see section "Robustness check"). This also suggests that uncertainty originating from the use of meteorological input data from the ERA5 model family likely does not affect our results to a large extent. However, bias in the meteorological input data that correlates with (e.g. seasonal) patterns in air concentrations would have a greater potential to distort IFM results. In contrast to substance ratios and f_{corr}, absolute deposition rates were found to be sensitive to changes in wind speed and IFM parameters (z_0, d, z_B, see section "Robustness check").

Another important source of uncertainty in our results originates from the restriction of air concentration measurements at Melpitz to PM_{10}, i.e. giant particles exceeding 10 µm diameter are not covered. We consider presence of Na^+ in giant particles unlikely at the Melpitz site (see Methods). For K^+, however, contribution from soil dust and fertilizer application with corresponding larger particle sizes has been mentioned to play a role at the Melpitz site (Spindler et al., 2010; Stieger et al., 2018). We address this issue by including only time periods in our study where PM_{10} concentrations probably reflect total air concentrations, i.e. by excluding periods affected by giant particles. We use monthly scavenging ratios (ω; based on the ratio of WD to PM_{10}) to identify months where high WD rates cannot be explained by corresponding PM_{10} concentrations, i.e. indicating presence of giant particles. The corresponding times series of monthly ω values (Online Resource S2.2) shows some joint peaks for K^+, Ca^{2+} and partly also Mg^{2+}, while ω for Na^+ stays on a low level. We consider it likely that these months are indeed affected by giant particles (e.g. soil dust). For other months, however, it is not obvious whether the detection approach for giant particle periods used in our study (see Online Resource S2) always yields the correct decision. Our results are sensitive to this classification of "giant particle periods" because WD_K during these months often contributes significantly to the annual WD rate of K^+. If all data is used (no exclusion of "giant particle periods"), f_{corr} changes from 1.66 to 1.29 (BL) and from 1.77 to 1.37 (CF). This means that the tendency of the CBM to underestimate DD_K remains but the magnitude is smaller. Calculations without giant particle filtering might be considered a lower boundary estimates of f_{corr} and are very likely at least to some extent biased by contribution of giant particles.

Another source of uncertainty regarding our results is the distribution of measured PM_{coarse} and PM_{fine} concentration among the six size bins used for DD modelling. We used data from an impactor study at the Melpitz site (Spindler et al., 2012) to allocate measured concentrations among size bins, with two important simplifications. First, our assignment of substance mass among size bins is static, although Spindler et al. (2012) report a dynamic stratification according to season and wind direction. Also, diurnal variations in PM concentrations (Stieger et al., 2018) and changes of particle size due to uptake of moisture (hygroscopic swelling) are not considered. Second, the relative allocation of measured daily PM_{fine} among the three PM_{fine} size bins is not substance-specific (the same applies for PM_{coarse}, see table S4.5). While these aspects contribute some uncertainty to our findings, the dominant pattern of particle size differences between substances (PM_{coarse}:PM_{fine} ratio of 1:3 for K^+ compared to 2:1 for Na^+) and its day-to-day variation is captured by our approach. In addition to the sources of uncertainty mentioned above, also the model variant used for DD calculations likely has effects on the resulting K^+:Na^+ ratios in DD. This is because the relation between particle size and v_d, and thus also the annual effective v_d calculated for smaller (e.g. K^+) and larger (e.g. Na^+) particles, differs between model variants (see for example Fig. 2 in Pleim et al. (2022)). We used a recent update (Emerson et al. 2020) of the common model by Zhang et al. (2001) for all calculations and did not investigate the structural uncertainty of the $DD^{(IFM)}$ results originating from the choice of the model among the many published IFM variants. Saylor et al. (2019) compared DD estimates from several IFMs and found differences of more than 200% between individual variants. These results cannot be interpreted in our context directly because they compared absolute DD rates and not the DD ratios of finer (e.g. K^+) vs. coarser (e.g. Na^+) particles. Nevertheless, their study suggests substantial uncertainty also in the IFM approach. A comparison of DD model variants with regards to K^+:Na^+ ratios in simulated DD would be an interesting endeavour but goes beyond the scope of this study.

Conclusion and outlook

In this study, we addressed the problem of limited validation for the widely used CBM approach for the calculation of base cation dry deposition. We found 66% - 77% higher rates of DD_K with a process-oriented inferential DD model (IFM) compared to $DD_K^{(CBM)}$. Considering the methodological uncertainties of the IFM, we interpret our findings as a potential indication but not as evidence of an underestimation of DD_K by the CBM approach. Correcting the CBM calculations for the potential underestimation of DD_K did not translate into large differences in quantities of ultimate interest at the five ICP Forests sites in the same region, like $DD_{\sum BC}$ or total N deposition. This is partly caused by the relatively low overall rates of DD_K (average annual rates between 0.32 and 1.23 kg ha^{-1} a^{-1}, depending on receptor (conifer vs. broadleaf forest) and method (IFM vs. CBM)). It is not clear, however, that this robustness of the CBM method in terms of $DD_{\sum BC}$ or total N deposition generalizes to other settings, for a number of reasons. First, we analysed only DD_K, but deviations might also appear for DD_{Ca} (which has important non-marine sources like soil dust with corresponding differences in particle size). Second, the relative importance of DD_K for total $DD_{\sum BC}$ or modelled N canopy uptake might be higher in other regions. Third, inter-annual changes in f_{corr} were partly driven by independent variation of WD_{Na} and Na^+ air concentrations, which points to the question to what extent WD concentration ratios reflect ground-level air concentration ratios, linked to the relative importance of rainout vs. washout. Fourth, the CBM has also been extended to other substances, like NH_4^+ (Ulrich, 1994) although NH_4^+ is, like K^+, mainly present in fine particles (Putaud et al., 2010, 2004). Bad performance of the CBM may translate more directly into errors in relevant quantities (like DD_{NH4}) in these extended applications of the CBM. These aspects suggest that neither our immediate findings (tendency for underestimation of the CBM) nor its consequences (small effects of applying f_{corr} on $DD_{\sum \mathrm{BC}}^{(CBM)}$ and $TD_{\mathrm{N}}^{(CBM)}$, at the five ICP Forests sites in the same region) can be easily generalized to other contexts. Thus, while our results support the idea that the CBM approach yields DD_K estimates in a roughly correct order of magnitude, more general conclusions about the performance of the CBM require further assessments. Options to replicate the approach used in our study at other sites are limited, as size- and chemically resolved air concentration measurements (especially including giant particles) are rare. Parallel sampling of substance ratios in WD and DD to surrogate surfaces could offer an alternative approach. For example, surrogate sampling based on Teflon strings under a roof has been successfully tested under a range of conditions (Ferm and Hultberg, 1999) and has recently been applied across Sweden (Karlsson et al., 2019). Our model results suggest a relatively high robustness of substance ratios in DD to variation in receptor properties (broadleaf, conifer, grassland), which supports the idea that surrogate sampler results can be transferred to other receptors like vegetation. Co-locating these simple and cheap devices at air quality measurement stations (like Melpitz) could yield additional insights regarding substance ratios in WD vs. aerosol vs. DD. More reliable DD_{BC} estimates at ICP Forests Level II sites could support large-scale (spatial) modelling of base cation dry deposition, which has remained challenging so far (Draaijers et al., 1996; Hellsten et al., 2007; Schaap et al., 2018; Tsyro et al., 2011).

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Statements and Declarations

Funding

Part of the data was Co-financed by the European Commission. Partial funding of data collection was provided by the European Union under Council Regulation (EEC) 3528/86 on the Protection of Forests Against Atmospheric Pollution, the Regulation (EC) 2152/2003 concerning monitoring of forests and environmental interactions in the community (Forest Focus) and by the project LIFE 07 ENV/D/000218 Further Development and Implementation of an EU-Level Forest Monitoring System (FutMon). Part of the work belongs to the project "Site adapted management in privately owned small forests" funded by BMEL/FNR (FKZ: 2220NR269C).

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Data Availability Statement

The meteorological input data used for the inferential modelling is freely available at the Climate Data Store (https://cds.climate.copernicus.eu). The EMEP air concentration and wet deposition data is freely available at the EBAS database (https://ebas.nilu.no). The ICP Forests Level II deposition data used for plausibility checks is available from the ICP Forests Programme Co-ordinating Centre (PCC) according to the ICP Forests data policy (http://icp-forests.net/page/data-requests).

Acknowledgements

The results contain modified Copernicus Climate Change Service information 2020. Neither the European Commission nor ECMWF is responsible for any use that may be made of the Copernicus information or data it contains. We thank the staff operating the Melpitz measurement station and organizing the data provision via the EBAS data portal. The evaluation of plausibility was mainly based on data that was collected by partners of the official UNECE ICP Forests Network (http://icp-forests.net/page/participating-countries). We thank the numerous staff involved in operating the intensive forest monitoring in Germany in the last decades, especially the staff of Brandenburg (LFB), Saxony-Anhalt (NW-FVA) and Saxony (Sachsenforst).

5. Synthesis

This chapter summarizes and discusses the results from the three studies conducted to fulfill the objectives of this PhD project:

1. Provide an overview of the responses of forest ecosystems in Europe to the decrease in N deposition that occurred in the last decades.
2. Provide a comparison of the background N deposition map from the German Environment Agency against in-situ measurements at forest monitoring stations.
3. Quantify the uncertainty in CBM-based N deposition estimates resulting from the assumption of similar K^+:Na^+ ratios in wet and dry deposition.

5.1 Responses of forest ecosystems in Europe to decreasing N deposition

Results from observational and experimental studies indicated that different domains of forest ecosystem parameters respond with different speeds to changes in N supply. Soil solution nitrate concentrations were found to be at the fast end of the response spectrum, with notable reactions to decreasing N deposition. At the other end of the spectrum, we found no signs of recovery of biodiversity status (understory vegetation) in Europe's forests in response to decreasing N deposition so far. Biodiversity patterns are expected to respond very slowly to changes in N supply, for example due to time lags in the colonization-extinction-dynamics of habitat patches. The different speeds of response are in line with the concept of pressure metrics, midpoint metrics and endpoint metrics suggested by Rowe et al. (2017) to track and communicate the effects of decreasing N deposition on ecosystems. Gilliam et al. (2019) emphasize that the development of forest ecosystem parameters during N de-saturation will not be a simple reversal of the trajectories during N enrichment (hysteresis behavior). Instead, time lags in ecological processes and slow nitrogen pools in soil compartments make the de-saturation harder to predict.

For tree nutrition (foliar N concentrations), some experimental studies suggest a relatively fast response to a reduction of N supply (with time lags of a few years). In line with these findings, some large-scale studies report decreasing trends in foliar N concentrations for the time period of decreasing N deposition in Europe (Jonard et al., 2015; Penuelas et al., 2020). However, at the same time, the foliar mass was found to be increasing, offering the 'dilution' of foliar N by increasing leaf or needle mass as an alternative explanation for the observed decrease in foliar N concentrations. Recently, this second explanation has gained support from an analysis by Penuelas et al. (2020), suggesting that increasing CO_2 concentrations boosted tree growth with an associated unmet nutrient demand, leading to a decrease in foliar concentrations of N and other nutrients, like phosphorus. Mason et al. (2022) even suggest a general decline of N availability in terrestrial ecosystems in Europe and North America. To the contrary, De Vries and Du (2022) argue that older time series from Europe (before the onset of the decrease of N deposition around 1990) typically report increasing instead of decreasing foliar N concentrations, although the CO_2 fertilization effect was already effective at that time. According to them, CO_2 fertilization could drive a reduction of foliar N concentrations in world regions with “stable and/or low levels of N deposition” but likely not in Europe. Further research is needed to determine the relative importance of the suggested mechanisms for the observed reduction in foliar N concentrations, given that the two explanations are not mutually exclusive and that N deposition shows a strong geographical variation across Europe (Ge et al., 2021). From a forest management perspective, the indications for critical tree nutrient supply status in some regions of Europe emphasize the need for harvesting strategies adapted to local conditions (Bolte et al., 2019). Ecosystem element budget calculations, taking into account local soil and hydrological conditions as well as atmospheric deposition rates, can serve as a tool for identifying sustainable harvest intensities that do not lead to nutrient depletion in the long term (Ahrends et al., 2022).

For forest growth, we found no evidence of a response to decreasing N deposition. Experimental and observational studies often suggest a unimodal response of tree growth to N deposition. For example, a recent study by Etzold et al. (2020) suggests that the maximum benefit of tree growth from N deposition is achieved at rates around 30 kg N ha^{-1} a^{-1} for some of the dominant tree species in Europe. The actual optimum N deposition rate for tree growth for a specific forest stand likely differs from this value depending on various factors like stocking density, climate, and soil conditions. Given that the decrease in N deposition across Europe was strongest in highly polluted areas, with little or no decrease in low polluted areas such as northern Scandinavia (Waldner et al., 2014), we hypothesize that the decrease in N deposition had small positive growth effects in very strongly polluted areas and negligible effects elsewhere.

We did not find large-scale responses of tree vitality (crown condition) to the decrease of N deposition. We hypothesize that effects like stand age (Eickenscheidt et al., 2016), drought (George et al., 2022), and insect attacks (Toïgo et al., 2020) complicate the detection of effects of changing N deposition on tree vitality. The other way around, vitality effects on N cycling in forests are likely, given the recent forest damages through drought and insect calamities (George et al., 2022; Rukh et al., 2023), which caused for example a heavy dieback of spruce in some regions of Germany (BMEL, 2022) and the Czech Republic (Hlásny et al., 2021). Considering that only little change in N emissions is expected in the next decades (Simpson et al., 2014), the fate of forest ecosystem N status will likely be determined by climate change and forest management during periods of forest growth (Borken and Matzner, 2009; Meesenburg et al., 2016) as well as during and after harvest or calamities (Vitousek, 1981).

5.2 Comparison of Methods for the Estimation of Total Inorganic Nitrogen Deposition to Forests in Germany

When considering the spatio-temporal average N deposition rate at around 100 German intensive forest monitoring stations between 2000 and 2016, we found slightly higher N deposition rates from the CBM (20.0 $\mathrm{kg\ N\ ha^{-1}\ a^{-1}}$, CBM according to Ulrich (1994)) compared to the background N deposition map (EBM approach) provided by the German Environment Agency (18.0 $\mathrm{kg\ N\ ha^{-1}\ a^{-1}}$, Schaap et al., 2018). The IFM approach led to deposition estimates exceeding the EBM by 2.7 - 6.3 $\mathrm{kg\ N\ ha^{-1}\ a^{-1}}$, depending on the IFM variant. Considering the complexities involved and the development of the background N deposition maps over the past decades (Schaap et al., 2018), this level of agreement between methods represents progress from a historical perspective. Nevertheless, several discrepancies between the background deposition map and N deposition estimates derived from in-situ measurements remain. For example, considering that certain deposition pathways are not fully captured in the CBM approach (especially the stomatal uptake of NH_3), we expected the order of methods in terms of N deposition to be CBM < IFM ≅ EBM, while we found EBM < CBM ≤ IFM. The observation of higher N deposition rates from the CBM compared to the EBM would also hold if other CBM variants had been used for comparison (De Vries et al., 2001; Draaijers and Erisman, 1995), as these yield on average higher deposition estimates compared to the Ulrich (1994) variant (Schmitz et al., 2017). This suggests a general tendency for underestimation of N deposition according to the EBM. Furthermore, we found that the average absolute difference of N deposition for a single plot and year between the EBM and the two in-situ methods was between 4.4 and 6.8 kg N ha^{-1} a^{-1} (depending on the method). If these differences between methods are interpreted as an indication of the uncertainty inherent in N deposition estimates, the reliability of current methods is not satisfactory, despite improvements from a historical perspective.

The analyses of differences between methods revealed that the mismatch between the EBM and the two in-situ-based methods was especially pronounced for DD at spruce plots. Both in-situ-based methods (CBM and IFM) point in the same direction regarding the differences to the EBM approach for spruce. This observation can be used to focus efforts on the improvement of methods more efficiently. Possible explanations are for example the disproportionate exposition of intensive monitoring sites in their respective EBM grid cells (1 x 1 km resolution) or problems with the correct representation of meteorological and/or receptor properties at spruce plots in the EBM. It should be noted, however, that the average absolute difference of N deposition for a specific plot and year between IFM and CBM is similar compared to the average absolute difference between CBM and EBM and differences among CBM variants are in a relevant magnitude as well. This means that even in-situ-based methods do not agree well on N deposition estimates and further improvements must be made in all methods.

5.3 Quantification of uncertainty in CBM-based N deposition estimates

As documented in chapter 4, we found differences between K^+:Na^+ ratios in measured WD and in DD simulated with an inferential DD model (DD^{IFM}), based on six years of data from the Melpitz research station in rural Germany. On average, the K^+:Na^+ ratio in WD was 0.24 while the K^+:Na^+ in DD^{IFM} was 0.43 (conifer forest, CF) and 0.4 (broadleaf forest, BL). Our results thus imply some deviations from the assumption of similar K^+:Na^+ ratios in WD and DD, underlying the CBM approach. This affects the various aspects of the CBM calculations to different extents. Most immediately, the CBM-based DD estimates for K^+ ($\mathrm{DD_K}^{\mathrm{CBM}}$) would need to be multiplied by an average correction factor of 1.66 (BL) and 1.77 (CF) to match $\mathrm{DD_K}^{\mathrm{IFM}}$. If this tendency for an underestimation of K^+ deposition by the CBM is confirmed in other regions, consequences for sustainable nutrient management might arise in specific regions. For example, Ahrends et al. (2022) calculated nutrient balances of base cations under different harvest intensities at German National Forest Soil Inventory plots, using the CBM approach for estimating the atmospheric deposition. They found that nutrient balances were generally less problematic for K^+ compared to Mg^{2+} or Ca^{2+}, but high harvest intensities could lead to negative balances for K^+ in the Alps, the Black Forest, the Swabian Alb, and the sandy sites of the northern lowlands. Their study shows that a correct estimation of atmospheric deposition is especially relevant in regions where ecosystem nutrient inputs by weathering are low.

When applying the abovementioned correction factors to five ICP Forests intensive monitoring plots in the same region as the Melpitz research site, we found that subsequent calculation steps in the CBM approach were less affected. For example, the average annual DD sum of the base cations K^+, Mg^{2+}, and Ca^{2+} ($DD_{\sum BC}^{CBM}$) increased by at most 22% when applying the correction factor for K^+. The implications of the correction of K^+ deposition for the assessment of the acid-base status at these plots are thus limited. $DD_{\sum BC}^{CBM}$ is also required for calculating the canopy uptake of N in the CBM variants after Draaijers and Erisman (1995) and De Vries et al. (2001). Applying the abovementioned correction factor for K^+ at the five ICP Forests plots reduced the calculated canopy uptake of N by at most 9%. This in turn decreased total inorganic N deposition according to the CBM (De Vries et al., 2001) by less than 2% on all plots. The effect on N deposition was small because canopy uptake accounted for only 13-21% of total inorganic N deposition at the five plots. Our results thus suggest that the deviations from the CBM assumption of similar K^+:Na^+ ratios in DD and WD do not induce large errors in the resulting N deposition estimates in the study region.

The modeled K^+:Na^+ ratios in DD^{IFM}, and thus also the (limited) consequences for $DD_{\sum BC}$ and total inorganic N deposition, were robust to variations in meteorological parameters and receptor properties. By contrast, periods potentially affected by soil dust re-suspension were an important source of uncertainty. During these periods, particles larger than 10 µm in diameter (“giant particles”), which are not captured by local air quality measurements, could have contributed a substantial fraction to the total suspended K^+ concentration. Therefore, seven months (10% of data) potentially affected by this problem were excluded from the analyses. When repeating the analyses without this data cleaning step, i.e. with all periods included, the correction factors for $\mathrm{DD_K}^{\mathrm{CBM}}$ reduced from 1.66 to 1.29 (BL) and from 1.77 to 1.37 (CF). Correspondingly, the tendency of the CBM to underestimate DD_K remained but on a smaller level. A third source of uncertainty results from the choice of the DD model. We used the state-of-the-art particle DD model suggested by Emerson et al. (2020), which is a re-parametrization of the widely used DD model by Zhang et al. (2001). However, DD model development is an active field of research (e.g. Pleim et al., 2022) and considerable variation between existing models has been reported (Saylor et al., 2019). In this sense, our results only yield a limited perspective on the question of substance ratios in DD compared to WD. We therefore consider our results an indication but not evidence for an underestimation of DD_K by the CBM.

Further progress could be made following three lines of research. First, existing data at other air quality monitoring stations (besides Melpitz) could be analyzed analogously to this study in cooperation with local experts, taking into account the limited representativity of PM_{10} due to the potential presence of giant particles. Second, analyses with an ensemble of DD models could yield a more comprehensive picture of the uncertainty resulting from different formulations of the particle DD process. Third, additional measurements at EMEP and/or ICP Forests sites with cheap and easy-to-operate surrogate samplers (e.g. Karlsson et al., 2019) could determine substance ratios in DD directly, thereby overcoming the problems of giant particles and DD modelling uncertainty. Results from such endeavors could feed into a quantification of the total uncertainty in the CBM approach, in combination with findings on the inertness of the tracer substance (e.g. Thimonier et al., 2008) and on the canopy exchange behavior of BC, N, and organic acids (Mohr et al., 2005).

5.4 Conclusions

Despite decades of research on the dynamics and effects of N in Europe's forest ecosystems, important research gaps remain. In this context, this dissertation adds three pieces to the pile of existing knowledge. First, we provide a summary of the responses of forest ecosystems in Europe to decreasing N deposition. We highlight that some ecosystem parameters respond quickly while the reaction of others would probably require more pronounced pollution reduction efforts over longer time periods. Furthermore, ecosystem responses are heterogeneous in space across Europe, depending on factors like the absolute level of air pollution, the magnitude of the deposition reduction, and site-specific factors. Correspondingly, a detailed monitoring of ecosystem responses to decreasing N deposition is required to track the success or failure of clean air policies and provide forest managers with information for long-term planning decisions. Second, we provide a comparison of the background N deposition data from the German Environment Agency against in-situ measurements at forest monitoring stations. We conclude that considerable differences between methods remain, which are especially pronounced for specific strata of sites. Further research is needed to arrive at cost-effective and reliable N deposition estimates for forests. Third, we contribute to characterizing the robustness of the CBM approach, which is one of the methods for calculating N deposition from in-situ measurements. We conclude that N deposition estimates are robust against deviations from one of the assumptions underlying the CBM approach in the study region. Further work is required to check whether these results generalize to regions with different atmospheric conditions. A comprehensive characterization of the robustness of the CBM approach would enhance the informative value of the data continuously collected at intensive forest monitoring sites across Europe. The need for such data as a foundation for the effective design and enforcement of clean air policy and for provident decision making in forest management will likely remain, considering that only little future change in N emissions is expected according to current legislation.

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Declaration of originality and confirmation of conformance

Recklinghausen, 15.04.2023

I, Andreas Schmitz, hereby declare that I am the sole author of this dissertation entitled "*Dynamics and effects of nitrogen in European forest ecosystems*". All references and data sources that were used in the dissertation have been appropriately acknowledged.

I furthermore declare that this work has not been submitted elsewhere in any form as part of another dissertation procedure.

Moreover, I confirm that the contents of the digital version are identical with the written scientific treatise.

Andreas Schmitz

Contribution of the doctoral candidate to the publications

This section summarizes the doctoral candidate's contribution to the cumulative dissertation's three publications.

First article: Schmitz A, Sanders TGM, Bolte A, Bussotti F, Dirnböck T, Johnson J, Peñuelas J, et al. Responses of forest ecosystems in Europe to decreasing nitrogen deposition. Environmental Pollution 2019;244:980–994.

- Design of the study
- Coordination of the team
- Literature review (observational and experimental studies)
- Writing and reviewing
- Submission/Publication

Second article: Ahrends B, Schmitz A, Prescher A-K, Wehberg J, Geupel M, Andreae H, Meesenburg H. Comparison of Methods for the Estimation of Total Inorganic Nitrogen Deposition to Forests in Germany. Frontiers in Forests and Global Change 2020;3:103.

- Design of the study
- Implementation of methods
- Data preparation and analyses
- Writing and reviewing

Third article: Schmitz, A., Ahrends, B., Herrmann, H., Moravek, A., Poulain, L., Sanders, T.G.M., Wiedensohler, A., Bolte, A. Underestimation of potassium in forest dry deposition? – A simulation experiment in rural Germany.

- Design of the study
- Coordination of the team
- Data acquisition, preparation and analyses
- Writing and reviewing

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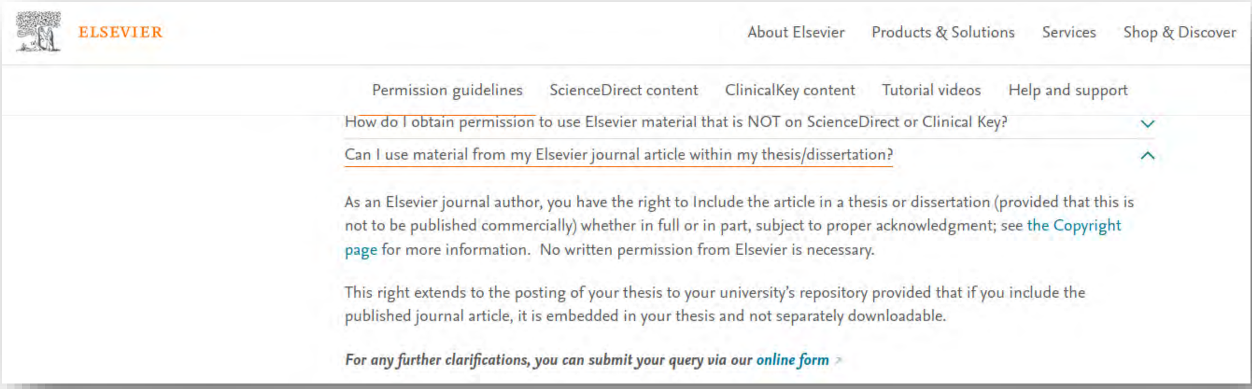

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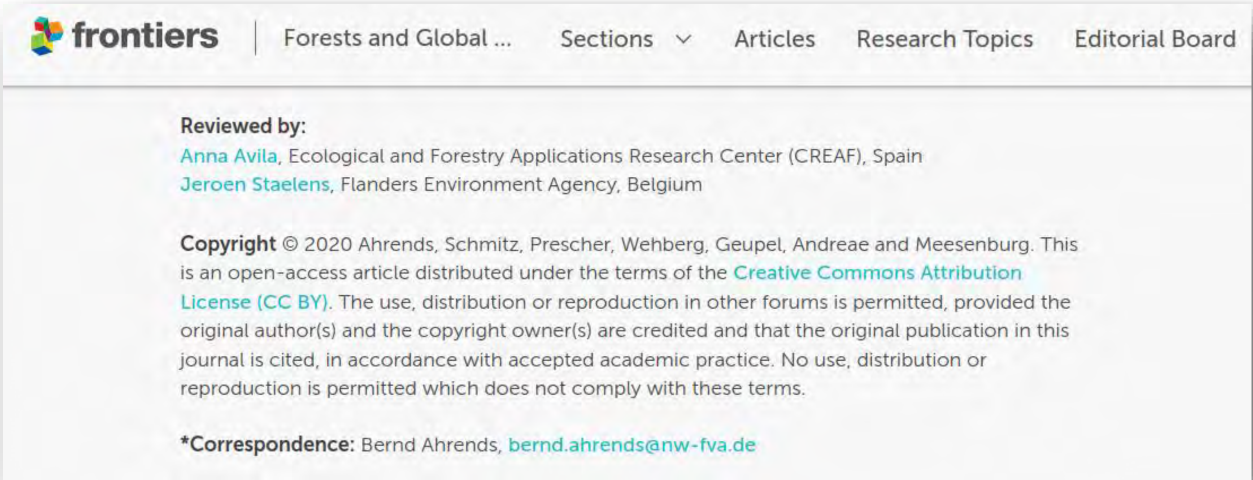

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The third article

Schmitz, A., Ahrends, B., Herrmann, H., Moravek, A., Poulain, L., Sanders, T.G.M., Wiedensohler, A., Bolte, A. Underestimation of potassium in forest dry deposition? – A simulation experiment in rural Germany

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Acknowledgements

Bedanken möchte ich mich…

… bei Prof. Dr. Andreas Bolte, Prof. Dr. Norbert Lamersdorf und Dr. Tanja Sanders für die freundliche und hilfreiche Unterstützung bei der Promotion.

… bei Prof. Dr. Heinz Flessa für die Bereitschaft der Disputation als Prüfer beizuwohnen.

… bei Bernd Ahrends und Thomas Gauger für den spannenden fachlichen Austausch in den letzten Jahren.

… bei Henning Andreae und den anderen Kolleginnen und Kollegen des Forstlichen Umweltmonitorings für die freundliche und konstruktive Atmosphäre in der Community.

… bei Britta Acksel für die mentale Unterstützung.

… bei meinen Eltern.

Curriculum vitae

Andreas Schmitz

Education

- 2004: Abitur, Carl-Fuhlrott-Gymnasium, Wuppertal
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Professional experience

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- 2016 - 2020: Thünen-Institute of Forest Ecosystems, Scientist
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Appendix to chapter 4

Supplementary Information (SI) to

Title: Underestimation of potassium in forest dry deposition? – A simulation experiment in rural Germany

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Supplementary material 1: Air concentrations after filtering and gap filling

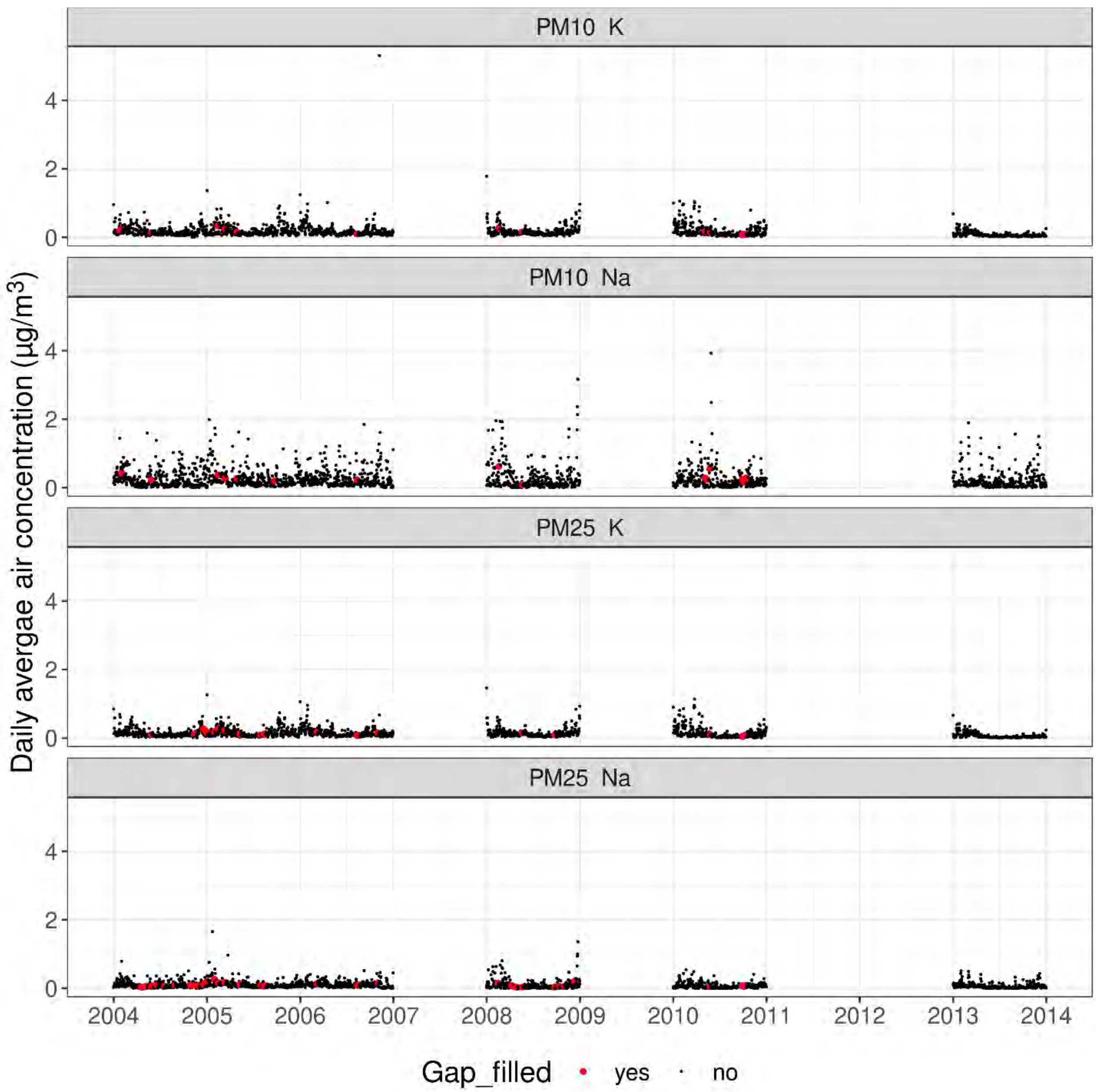

Fig. S1 Time-series of $PM_{2.5}$ and PM_{10} concentration measurements at the Melpitz site for the six years with sufficient data coverage. Red dots indicate days where hours not covered by measurements have been gap-filled

Supplementary material 2: Filtering for giant particles

This section describes the identification of periods potentially affected by the presence of K^+-containing giant particles (e.g. from soil dust). It is based on the assumption that such periods will be characterized by elevated scavenging ratios (ω, ratio of concentrations in precipitation vs. PM_{10}), because giant particles are easily scavenged by precipitation but missing in PM_{10} data. The approach is conducted in three steps: (1) Calculation of scavenging rates ω, (2) identification of a threshold level (ω*) above which relevant contribution from giant particles is suspected, and (3) exclusion of periods where the scavenging ratio of K^+ (ω_K) exceeds the threshold ($\omega_K > \omega^*$).

1. Calculation of scavenging ratios

We calculated ω according to eq. 3 (see section “Air concentrations”) in the main text. In order to make ω comparable between substances, we correct ω for differences in particle size. This is necessary as scavenging of fine particles is less efficient compared to scavenging of coarse (and giant) particles (Wang et al., 2010). We implement this correction by calculating c_{air} as:

$$c_{air} = c_{PMcoare} + 0.5\ c_{PMfine}$$

The correction factor for PM_{fine} is based on a literature review on the relative scavenging efficiency of fine vs. coarse particles (Table S2), indicating that empirical studies typical report a ω_{fine}:ω_{coarse} ratio of around 0.5 (despite considerable variations). Following Cheng and Zhang (2017), we calculate ω on a monthly basis in order to reduce noise and account for the fact that WD data is not available each week (especially in the summer month). I.e. ω is calculated from monthly volume-weighted average precipitation concentrations and monthly average PM_{coarse} and corrected PM_{fine} concentrations.

Table S2: Literature review of empirical scavenging ratios for PM_{fine} and PM_{coarse}. Column „$\omega_{fine}/\omega_{oarse}$" indicates the ratio of scavenging ratios for fine vs. coarse particles. Abbreviated references refer to: ZH21 (Zhou et al., 2021); BA18 (Blanco-Alegre et al., 2018); CH21 (Cheng et al., 2021); CZ17: (Cheng and Zhang, 2017)

Ref.	ω_{fine}/ ω_{coarse}	Precip. intensity (mm/h)	Precip. duration (h)	Type	Location	Sampling duration	Comment
ZH21	0.48	10	Average over many observed rain events	Below-cloud scavening	1 plot in China	4 years	Based on absolute air concentration loss rates
BA18	0.47	independent	1	Below-cloud scavening	1 plot in Spain	7 month	Converted from reported scavenging efficiency
BA18	0.57	independent	5	Below-cloud scavening	1 plot in Spain	7 month	Converted from reported scavenging efficiency
CH21	0	broad meta-analyses		Total scavenging	Global	variable	Extracted from regression line in Fig. 2c
CZ17	Plot-wise median: 0.35 - 0.85; median over plots: 0.6	multiple plots & years		Total scavenging	13 plots in Canada	Multiple years per plot	Direct calculation from parallel particle and WD measurements

2. Identification of a threshold level for scavenging ratios (ω^*)

We consider ω_{Na} not to be affected by giant particles (see section "Air concentrations" in main text), i.e. the monthly values of ω_{Na} are indicative for scavenging ratios not affected by giant particles. We assume there is a typical level of variation ($\Delta\omega$) around ω_{Na}, such that scavenging ratios of K^+ are considered "unusually high" only if $\omega_K > \omega^*$ with $\omega^* = \omega_{Na} + \Delta\omega$. We use the variation between monthly pairs of ω_{Na} and ω_{Mg} in winter to get a rough estimate of the magnitude of the typical level of variation ($\Delta\omega$), because these two substances show a consistent pattern during winter, indicating conditions unaffected by giant particles (Fig. S2.1). Specifically, we calculate $\Delta\omega = 1706$ as the 95% quantile of the absolute differences between monthly pairs of ω_{Na} and ω_{Mg} values in winter.

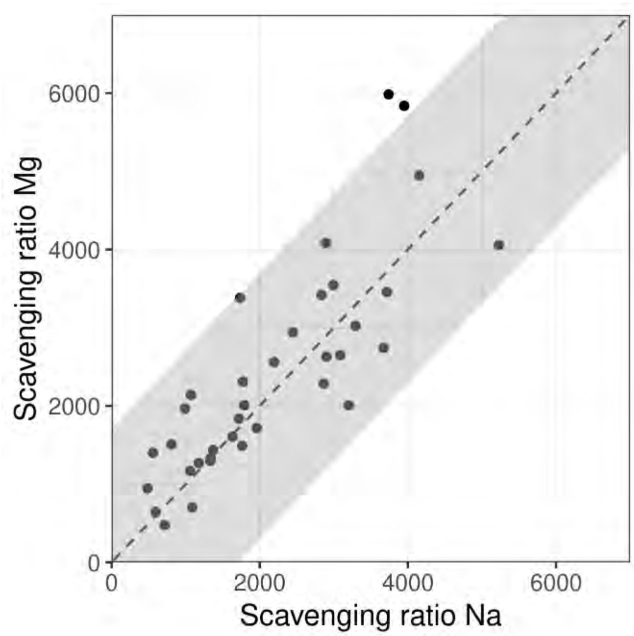

Fig. S2.1 Consistent relationship between monthly scavenging ratios (ω) of Mg^{2+} and Na^+ in winter. The dashed line is a 1:1 line. The variability between ω_{Na} and ω_{Mg} is considered the "typical variability" for ω and is used for the outlier classification of K^+. The grey area reflects this typical level of variation ($\Delta\omega = 1706$, see text).

3. Exclusion of periods where the scavenging ratio of K^+ exceeds the threshold

According to the procedure described above, 7 months with $\omega_K > \omega^*$ are identified and excluded from further analyses. The time series of ω and resulting outlier classification for K^+ is shown in Fig. S2.2. All excluded months are in the period Mai - October and elevated ω_K often coincides with elevated ω_{Ca} and partly also ω_{Mg}, suggesting a common origin, i.e. likely soil particles.

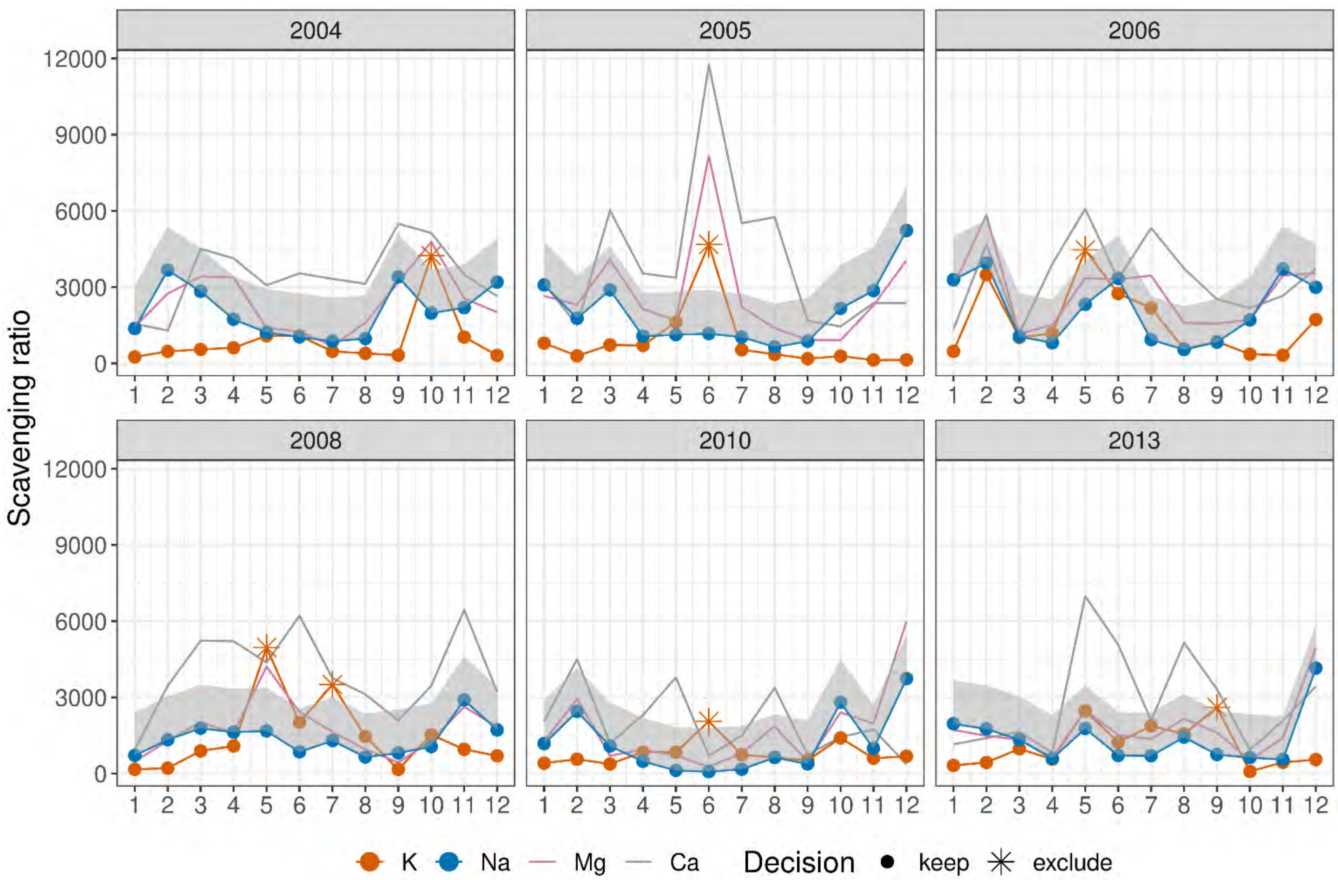

Fig S2.2 Monthly scavenging ratios. The grey area reflects the typical level of variation added on top of ω_{Na} (bounded by $\omega^* = \omega_{Na} + \Delta\omega$ with $\Delta\omega = 1706$). Months when ω_K exceeds ω^* are considered to be affected by giant particles and excluded from further analyses (Decision = "exclude"). Time series for Mg^{2+} and Ca^{2+} are shown to highlight co-occurrence of elevated ω for several substances in summer, potentially due to common origin from soil particles

Supplementary material 3: Wet deposition time series

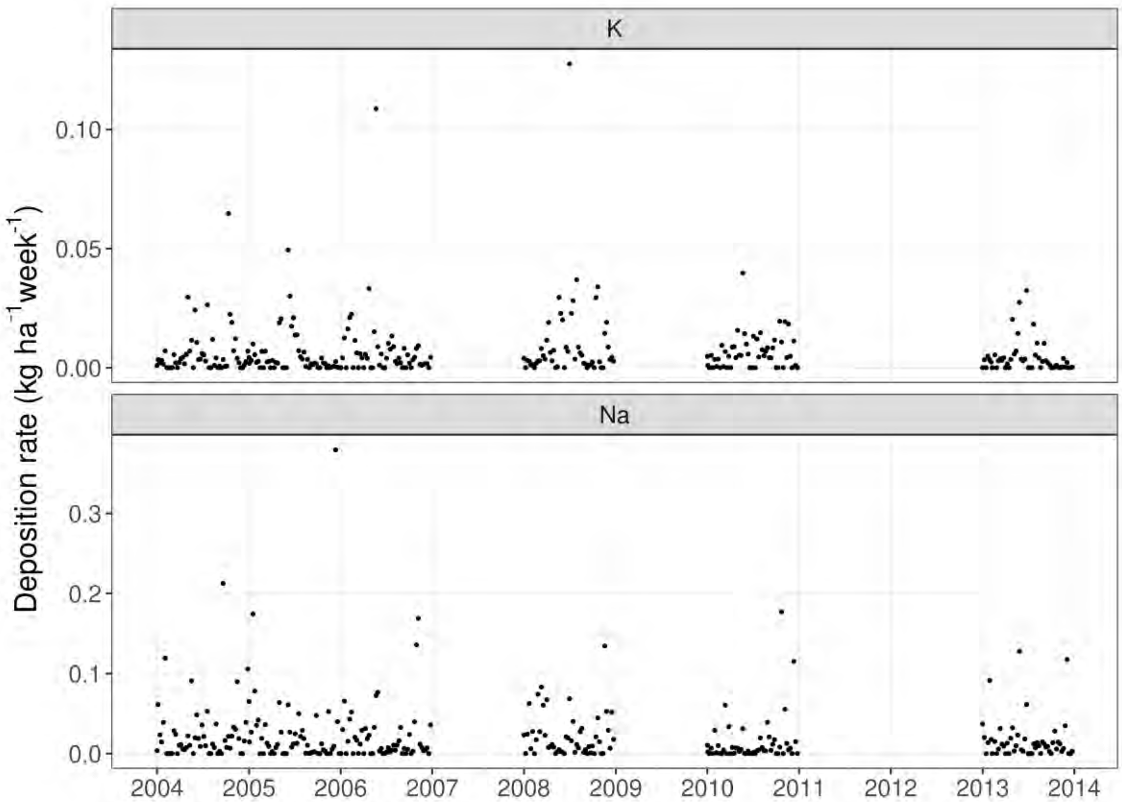

Fig. S3 Time-series of weekly wet deposition measurements at the Melpitz site for the six years studied

Supplementary material 4: Detailed description of the inferential modelling (IFM) procedures

Aerodynamic resistance R_a

The aerodynamic resistance describes the atmospheric transport of particles from the reference height where concentrations are available (z_M and z_b) to the effective height of the receptor surface (given by the sum of roughness length z_0 displacement height d) (Erisman and Draaijers, 1995). As R_a depends on the receptor surface, we calculated $R_a^{(M)}$, $R_a^{(BL)}$ and $R_a^{(CF)}$ separately for each of the three receptor surfaces (grassland measurement site M, and the two indicator forest types). The calculation of R_a is performed in two parts. The individual calculation steps are implemented according to standard procedures described in Erisman and Draaijers (1995) and Seinfeld and Pandis (2006).

First, we extrapolate the wind speed at 10 m height from the ERA5 model to the wind speed at z_b (50 m) using a stability-corrected vertical wind profile. The individual steps are: (a) Calculate the Pasquill class that roughly describes the general atmospheric stability conditions, based on wind speed at 10 m height, global radiation, cloud cover and time of day (day or night). (b) Calculate the Monin–Obukhov length that characterises atmospheric turbulence from the Pasquill class and the z_0. The roughness length for which the ERA5 wind data has been calculated is for grassland conditions (z_0 = 0.03 m, ECMWF (2021)). We assume a corresponding displacement height d = 0.21 m (7 x z_0, Simpson et al. 2012). (c) Calculate the friction velocity at “anemometer height” (10 m for the ERA5 wind data), based on wind speed, Monin–Obukhov, z_0 and d. (d) Extrapolate the wind speed to z_b using the stability-corrected vertical wind speed profile, based on friction velocity, Monin–Obukhov, z_0 and d.

Second, we calculate R_a for each receptor surface separately. The individual steps are: (a) Calculate the Monin–Obukhov length based on the general information on atmospheric stability (Pasquill class) and the z_0. We use the definition of z_0 for CF and BL after Zhang et al. (2001) depending on season. It ranges between 0.8 m and 0.9 m for CF and between 0.55 m and 1.05 m for BL. For the measurement site (grassland) we assume z_0 and d used for the wind speed calculations above. (b) Calculate friction velocity based on wind speed at z_b and Monin–Obukhov length, z_0 and d. For the two indicator forest types, we assume a displacement height of 78% of the tree height (Simpson et al., 2012). For tree height, we assume the average height of trees at the surrounding ICP Forests plots, resulting in d = 20.3 m. (c) Calculate R_a between z_b and z_0+d for the respective receptor based on friction velocity, Monin–Obukhov, z_0 and d.

Surface resistance Rs

The surface resistance R_s describes the deposition of particles on the receptor (leaf, needle, woody surface, etc.) given that they have been transported into the air layer close to the surface. Emerson et al. (2020) parametrize R_s by modelling the deposition process by Brownian diffusion, impaction and interception, correcting for a possible re-bounce of particles from dry surfaces. The corresponding equations and parameters are given in Emerson et al. (2020) and Zhang et al. (2001).

Gravitational settling v_g

The gravitational settling describes the sedimentation of particles and is mainly dependent on particle diameter and density. The corresponding equations are given in Zhang et al. (2001) and are used in the Emerson et al. (2020) without modifications.

Seasonality

Two parameters of the DD model (z_0 and the characteristic radius of the receptor, A) depend on season (Zhang et al. 2001). These parameters also reflect the difference in the leaf area index (LAI) between seasons and forest types. In order to define a timing (day of year) for the seasons listed in Zhang et al. (2001) that roughly matches conditions in Germany, we use phenological information for the dominant broadleaf species in Germany (European beech (Fagus sylvatica L.)) based on data from German ICP Forests Level II plots (table S4.1).

Table S4.1: Season codes and parameter values used in Emerson et al. (2020) as well as the timing selected for application at the Melpitz site (A: Characteristic radius, z_0: Roughness length). No seasonal dependence is used for A for conifer forest (2 mm), A for grassland (10 mm) and z_0 for grassland (0.03 m). BL: Broadleaved forest, CF: Coniferous forest, DOY: Day of year

Season Code	**Season**	**z_0 BL (m)**	**z_0 CF (m)**	**A BL (mm)**	**Date period**	**Calculation rule**
1	Summer	1.05	0.8	5	14.5. - 18.9.	Between spring and early autumn
2	Early autumn	1.05	0.9	5	19.9. - 18.10.	The month before start of late autumn
3	Late autumn	0.95	0.9	10	19.10. - 18.11.	One month centred on the average DOY of leaf fall
4	Winter	0.55	0.9	10	19.11. - 13.4.	Between late autumn and spring
5	Spring	0.75	0.8	5	14.4. - 13.5.	One month centred on the average DOY of leaf flushing

Particle size distribution

The calculations of v_d with the resistance framework depend on particle size. We distribute the measured PM_{10} and $PM_{2.5}$ concentrations into six particle size bins, derived from results of a 5-stage impactor study at the measurement site (Spindler et al., 2012). v_d calculations are then conducted for each of the six size classes. In detail, we proceeded as follows. As a first step, we calculated the PM_{coarse} concentration as the difference between PM_{10} and $PM_{2.5}$. If the difference was negative, we assumed the PM_{coarse} concentration was negligible and used a value of zero. In the following, we refer to $PM_{2.5}$ as PM_{fine}. Second, we established the distribution of PM_{coarse} and PM_{fine} concentration among the six size bins. To this end, we extracted the PM_{10} concentration shares (%) of the 5 size bins from Fig. 2 in Spindler et al. (2012). The study is based on data from 169 measurement days with a Berner impactor between 2004 and 2009, stratified by wind direction and season. Bins A, B and C are entirely within the PM_{fine} range, but bin D overlaps the PM_{fine} border (diameter range: 1.2 µm - 3.5 µm) (see table S4.2).

Table S4.2: Concentration shares (%) per size bin for different seasons and wind directions (WiW: winter west, SuW: summer west, WiE: winter east, SuE: summer east). Original data from Fig. 2 in Spindler et al. (2012)

Bin	Lower bin diameter (µm)	Upper bin diameter (µm)	WiW	SuW	WiE	SuE
A	0.05	0.14	3	6	4	6
B	0.14	0.42	23	28	20	33
C	0.42	1.2	53	37	63	41
D	1.2	3.5	17	18	11	11
E	3.5	10	4	11	2	9

To allow for distributing measured PM_{fine} and PM_{coarse} among the bins, we split bin D at 2.5 µm into two new bins (D1 and D2) and distributed the relative mass shares of bin D among D1 and D2 proportionally to their respective bin width (Table S4.3).

Table S4.3: Adjusted concentration shares (%) after splitting bin D

Bin	Lower bin diameter (µm)	Upper bin diameter (µm)	WiW	SuW	WiE	SuE
A	0.05	0.14	3	6	4	6
B	0.14	0.42	23	28	20	33
C	0.42	1.2	53	37	63	41
D1	1.2	2.5	10	10	6	6
D2	2.5	3.5	7	8	5	5
E	3.5	10	4	11	2	9

We then converted the concentration share of each bin among PM_{10} to the mass share among its respective PM class (e.g. share of bin A among PM_{fine}, share of bin D2 among PM_{coarse}, etc., see table S4.4).

Table S4.4: Concentration shares (%) of bins A-D1 among PM_{fine} and concentration shares of bins D2 and E among PM_{coarse}

Bin	PMClass	Lower bin diameter (µm)	Upper bin diameter (µm)	WiW	SuW	WiE	SuE
A	PM_{fine}	0.05	0.14	3	7	4	7
B	PM_{fine}	0.14	0.42	26	35	22	38
C	PM_{fine}	0.42	1.2	60	46	68	48
D1	PM_{fine}	1.2	2.5	11	12	6	7
D2	PM_{coarse}	2.5	3.5	64	42	71	36
E	PM_{coarse}	3.5	10	36	58	29	64

Finally, we averaged the resulting PM_{coarse} and PM_{fine} related concentration shares over wind direction and season because the concentration shares were mostly similar across different combinations of season and wind direction. The centre of each bin (µm) was then used as diameter for the respective v_d calculation. The resulting concentration shares are shown in table S4.5. The resulting seasonal average air concentrations per size bin are shown in Fig. S4.1. We use a density of 1600 kg m^{-3} for PM_{fine} and 2200 kg m^{-3} for PM_{coarse} (Simpson et al. 2012).

Table S4.5: Distribution of concentration in PM_{fine} among bins A - D1 and distribution of concentration in PM_{coarse} among bins D2 and E

Bin	PM class	Concentration share among PM class (%)	Bin diameter centre (µm)	Lower bin diameter (µm)	Upper bin diameter (µm)
A	PM_{fine}	5	0.095	0.05	0.14
B	PM_{fine}	30	0.28	0.14	0.42
C	PM_{fine}	56	0.81	0.42	1.2
D1	PM_{fine}	9	1.85	1.2	2.5
D2	PM_{coarse}	53	3	2.5	3.5
E	PM_{coarse}	47	6.75	3.5	10

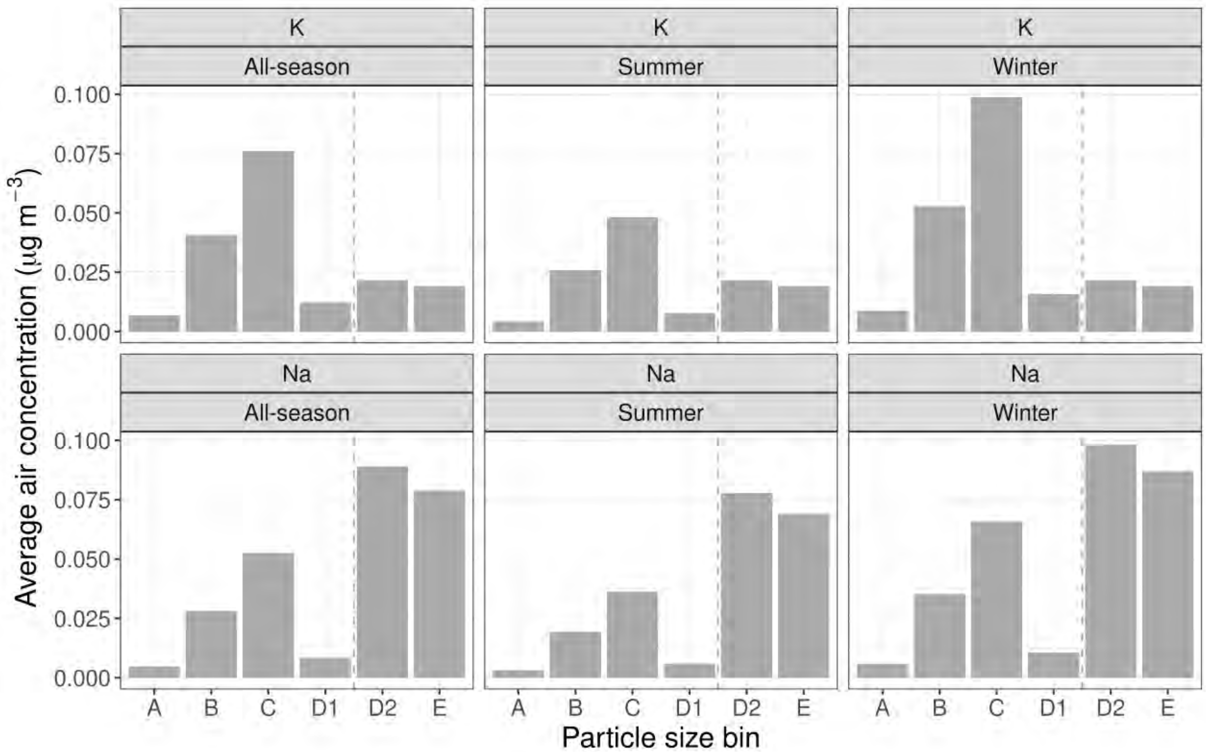

Fig. S4.1 Average K^+ and Na^+ concentration per particle size bin, resulting from distributing the daily measured PM_{fine} and PM_{coarse} concentrations among the six size bins according to table S4.5. The vertical dashed line separates PM_{Fine} (<2.5 µm, bins A-D1) from PM_{Coarse} (>2.5 µm, bins D2 and E). Following Spindler et al. (2012), winter is defined as the period from November to April. Elevated K^+ concentrations in PM_{fine} in winter likely result from domestic heating (Spindler et al., 2012). Higher Na^+ concentrations in winter in both size ranges (coarse and fine) are probably caused by increased sea salt emission and transport due to typically higher wind speeds in winter (Tsyro et al., 2011)

Overview of IFM parameters

Table S4.6: Parameters used for the IFM

Symbol	Parameter name	Parametrization (value)			Unit	Reference
		Grass	Conifer	Broadleaf		
z_0	Roughness length	0.03	See table S4.1		m	Simpson et al. (2012), Zhang et al. (2001)
d	Displacement height	0.21	20.3	20.3	m	Simpson et al. (2012)
A	Characteristic receptor radius	10	2	See table S4.1	mm	Emerson et al. (2020)
-	Surface wetness	True if relative humidity > 85%			bool	Burkhardt et al. (2009)
z_{ref}	Reference height	1.5 and z_b	z_b	z_b	m	Spindler et al. (2004)
z_b	Blending height	50			m	Erisman and Draaijers (1995)
-	Particle density	1600 (PM_{fine}) and 2200 (PM_{Coarse})			kg m^{-3}	Simpson et al. (2012)
d_p	Particle diameter	See table S4.5			µm	Spindler et al. (2012)
other	See "revised" parametrization as documented in Emerson et al. (2020) table S1 and Zhang et al. (2001) table 3.					

Verification of the implementation of the IFM

The implementation of the IFM has been tested by reproducing the graphs shown in Emerson et al. (2020). Figure S4.2 shows the contribution of the individual DD sub-processes (gravitational settling, Brownian diffusion, impaction, interception). Figure S4.3 shows the relation between DD velocity and particle size for the three land cover classes used in this study.

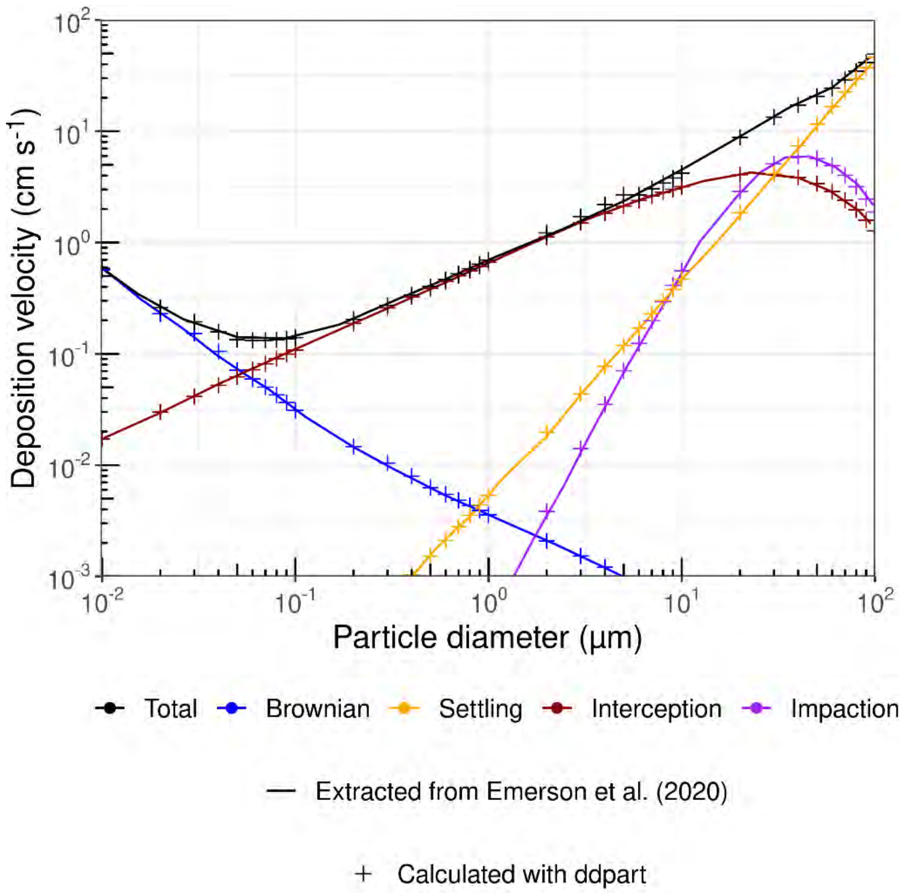

Fig. S4.2 Contribution of Brownian diffusion, gravitational settling, interception and impaction to the total DD velocity according to the Emerson et al. (2020) model. Lines indicate data extracted from Fig. 2 in Emerson et al. (2020). Results from the *ddpart* R package are indicated by "+". Results are shown for 0.4 m s^{-1} friction velocity, needleleaf forest, a particle density of 1500 kg m^{-3} and annual averages of season-dependent parameters. Data from *ddpart* is generated with aerodynamic resistance set to zero, no hygroscopic swelling and dry surface

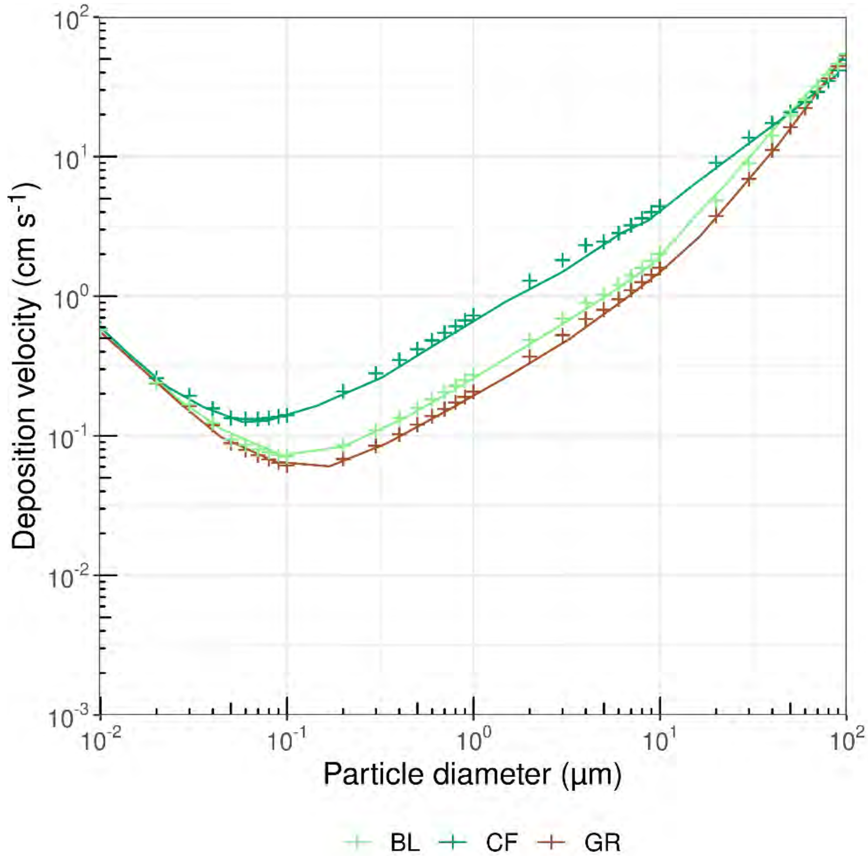

Fig. S4.3 Dry deposition velocity as a function of particle diameter for needleleaf forest, deciduous broadleaf forest and grassland. Lines represent data extracted from Fig. 1 in Emerson et al. (2020). Results from the *ddpart* R package are indicated by +. The figures show results at 0.4 m s^{-1} friction velocity and a particle density of 1200 kg m^{-3}. Data from *ddpart* is generated with aerodynamic resistance set to zero, dry surface, 80% relative humidity and corresponding hygroscopic swelling for aerosol of type 'rural' (eq. 10 in Zhang et al. (2001)). Particle diameter refers to the dry particle diameter (i.e. before accounting for hygroscopic swelling). Small differences are likely caused by imprecision of manual data extraction from Fig. 1 in Emerson et al. (2020)

Sensitivity check for the temporal resolution of air concentrations

Long-term $PM_{2.5}$ and PM_{10} concentration measurements at the Melpitz site are available at daily resolution. Dry deposition modelling is, however, conducted at an hourly time step. Therefore, daily concentrations are downscaled to hourly concentrations by assuming daily averages for each hour (see “Methods”). To check that this simple downsampling approach has only limited effects on the resulting deposition rates, we ran auxiliary simulations based on hourly PM_{10} data available from a separate measurement campaign in 2010. The corresponding data are freely available from the EBAS data portal (see section Data Availability Statement in the main text). In the “hourly” variant, we calculate deposition fluxes with the hourly data. In the “daily” variant, we first calculate the average daily concentration from the hourly data and then assign this daily concentration to each hour. As in the main analyses, we sum up the deposition fluxes over the year. We included only days with full coverage (24 hours of valid measurements), resulting in 17% (K^+) and 11% (Na^+) temporal coverage of the year 2010. Fig. S4.4 shows the sum of hourly deposition rates for the two indicator forest stands. The two approaches differ by around 5% at most (Na^+ deposition to the conifer indicator stand). We thus conclude that our approach of using daily average concentrations for each hour does not introduce a large bias in the resulting deposition sums.

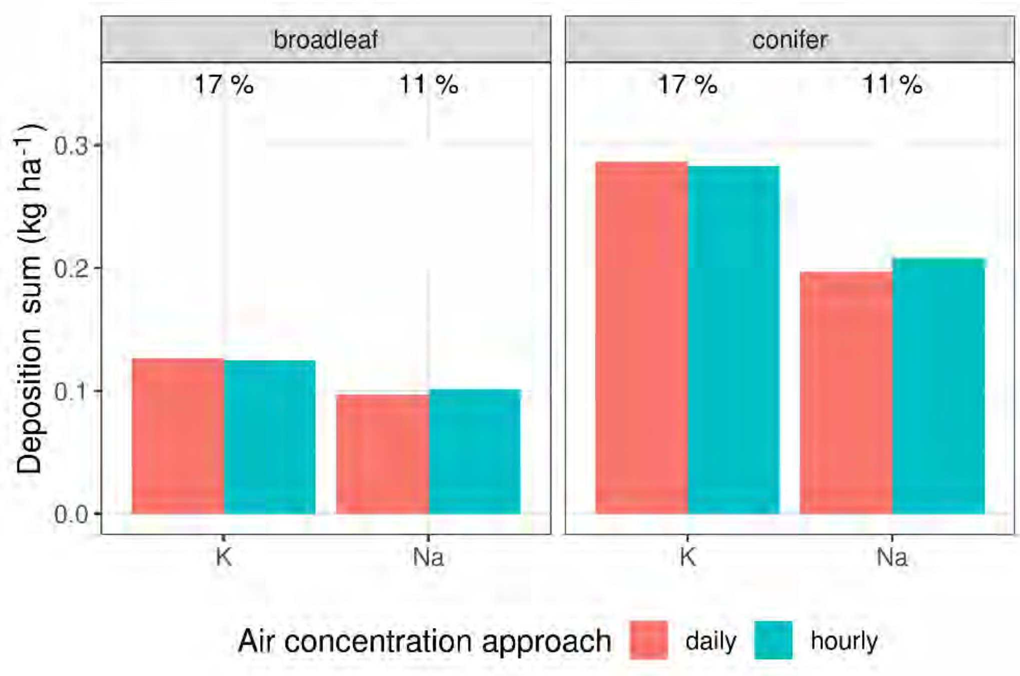

Fig. S4.4 Dry deposition sums of K^+ and Na^+ based on hourly measured (blue) and based on daily averages of hourly measured (red) PM_{10} concentrations. Only fully covered days (24 hourly measurements) in 2010 have been included in the comparison. The number of fully covered days differs between substances, numbers at the top indicate the annual coverage