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Assessing the contribution of soil NO_x emissions to European atmospheric pollution

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Abstract

Atmospheric NO_x concentrations are declining steadily due to successful abatement strategies predominantly targeting combustion sources. On the European continent, total NO_x emissions fell by 55% between 1990 and 2017, but only modest reductions were achieved from the agricultural sector; with 7.8% from 20 Eastern European countries and 19.1% from 22 Western European countries. Consequently, the share of agricultural NO_x emissions for these 42 European countries have increased from 3.6% to 7.2%. These values are highly uncertain due to serious lack of studies from agricultural soils and manure management. The emission factor (EF_{NO} 1.33%), currently used for calculating soil NO_x emissions from European agricultural categories 'N applied to soils' and 'manure management' was evaluated here by including recently published data from temperate climate zones. The newly calculated EF_{NO} (average 0.60%, $0.06_{25th\%}/0.54_{75th\%}$, $n = 65$ studies) is not notably different from the current value, given the large uncertainties associated with the small pool of studies, and therefore continued use of EF_{NO} (1.33%) is recommended until more data become available. An assessment of the contribution of agricultural and non-agricultural NO_x sources found that of the 42 European countries, the 8 most populated countries achieved considerable reductions (1990–2017) from categories 'non-agricultural sources' (55%), 'N applied to soils' (43%) and 'manure management' (1.2%), compared to small reductions from the remaining 34 countries. Forests are also large sources of soil NO_x. On average, emissions from Eastern European forests were 4 times larger than from 'N applied agricultural soil', whereas Western European NO_x emissions from 'N applied agricultural soil' were two times larger than from forest soils. Given that non-agricultural sources of NO_x continue to decline, soil related emissions from agriculture, forests and manure management become more important, and require rigorous investigation in order to improve atmospheric pollution forecasts.

1. Introduction

Nitric oxide (NO) is a main component of the nitrogen oxides (NO_x: $NO + NO_2$), a highly reactive and short-lived molecule, involved in the tropospheric chemistry of photochemical production of ozone (O_3) and aerosols, impacting on human health, global warming, crop production and eutrophication of vulnerable ecosystems.

Globally, combustion sources (fossil fuel, biomass and biofuel burning and wildfires) account for 76% of total NO_x emissions. Soils contribute 20% (natural soils account for 12% and agricultural soils for 8%), and aviation and lightning around 4% [1, 2].

It is estimated that 4%–8% of the total EU 27 annual NO_x emissions originate from nitrogen (N) fertilised agricultural soils [3]. On hot summer days, however, NO_x emissions from N fertilised soils may contribute up to 27% of total NO_x emissions [4]. Soil NO_x emissions arising from N fertilisation are of particular importance in rural areas, where traffic and stationary combustion sources are small, so agricultural emissions play an important role in rural air pollution, especially O_3 production [5, 6]. Increased O_3 concentrations are known to reduce crop production and forest growth [7].

In soils, NO is produced microbially and abiotically. The main microbial pathways responsible for NO production are nitrification and denitrification [8] and other recently discovered processes [6, 9]. The same groups of microorganisms involved in nitrous oxide (N_2O) production are also responsible for NO emissions and uptake. Key drivers, which influence soil NO and N_2O emission rates are: (a) the nature and magnitude of the N source, i.e. fertilisers, manures, mineralisation of organic matter, atmospheric N deposition; (b) the degree of soil aeration, which is controlled by soil texture, bulk density, precipitation and microbial activity; (c) temperature, which determines the rate of enzymatic reactions [10]; and (d) soil pH, which influences the role of abiotic and biotic NO production pathways [6]. Largest soil NO emissions occur in dry, well-drained and low organic matter content soils and the opposite is the case for N_2O [11], although increasing the N supply and temperature increases the production of both gases. Abiotic production may occur in soils with high organic matter content and acid soils [12]. The importance of abiotic NO production relative to microbial production is largely unknown, and poorly investigated [9, 13]. Concerted efforts in Europe and many other countries have led to large reductions in NO_x emissions from combustion sources. By 2017, the EU28 countries achieved an overall 58% reduction compared to 1990 levels [14]. Emissions from the agricultural sector also declined, but at much lower rates [14]. If this trend continues, the contribution of soil NO_x emissions from the agricultural sector will become a major source. For example, in California significant reductions of combustion sources have led to soil NO_x emissions being the major source of atmospheric NO_x pollution [15].

The aim of this paper is to (a) evaluate current approaches to calculate soil NO_x emissions, and (b) investigate changes in total and soil NO_x concentrations for the European continent.

2. Methods

2.1. Calculation of soil NO emission rates and emission factors (EFs) for temperate climate zones

In this paper we will use the term 'NO' for microbial processes and EFs, and the general term 'NO_x' when comparing different categories of NO_x, which are presented as NO_2, as prescribed by the European Environment Agency (EEA) [3].

Soil NO fertiliser/manure induced emission factors (EF_{NO}) and emission rates were calculated from a global meta-analysis for the period 1988–2016 [16].

EFs for NO-N are derived from the percentage of soil NO-N emission rates in relation to fertiliser N application rates, and here labelled as EF_{NO}. Liu's dataset was filtered for temperate climate zones and managed crop and grasslands. Other relevant datasets, not included by Liu *et al* [16] were added [17–23]. A total of 43 studies were selected and provided 129 data from the European continent (n = 49), North America (n = 30), Japan (n = 43) and China (n = 7). Rates and categories of N fertilisers and cumulative soil NO fluxes were available from crops (n = 102), grasslands (n = 27), and background emissions (zero N application, n = 27) (table 1). Most studies applied synthetic N fertilisers (n = 98), such as urea, ammonium nitrate and ammonium sulphate with and without other N compounds, nutrients and nitrification inhibitors. Only 31 data sets included manures (i.e. cattle, pig, poultry manures, treated and untreated slurries). Synthetic N fertiliser application rates >400 kg N ha^{-1} were excluded; as such high rates are not widely used by farmers. The data are from plot experiments, investigating different treatments and from observations. They range from 20 to 570 d, with an average study period of 176 d. In addition, six short-term data (20, 21 d) were included as they specifically focused on the response of soil NO emissions, before and after N fertilisation [18–23]. Many of these studies also measured soil N_2O emissions (n = 103), of which 73 data were fertilised with synthetic N and 30 with manures. These N_2O data were included in the overall data analysis. In the case of NO, the EF_{NO} were calculated as a percentage of the N input, with and without background emissions.

In order to compare soil NO emissions from crop and grasslands with those from forest soils, we calculated forest soil NO emission rates based on published data from temperate climate forests (n = 30) [16, 24, 25].

2.2. Calculating the contribution of soil NO_x emissions to total NO_x emissions for the European continent

Time series of agricultural and non-agricultural NO_x emissions were obtained for the 42 European countries and divided into East/West geographical regions. Western Europe includes the former EU15 countries plus Cyprus, Iceland, Lichtenstein, Malta, Monaco, Norway and Switzerland (n = 22). Of the 24 Central and East European countries Armenia, Azerbaijan, Georgia and Kosovo were excluded (n = 20) [26]. Officially reported NO_x emissions (using the 2014 reporting guidelines) were downloaded for the years 1990–2017 from the EMEP database and using GNFR (Gridding nomenclature for reporting) reporting levels [26]. The categories used were: (a) 'K_AgriLivestock', which is manure management from dairy, sheep, pigs, and other farm animal manures; (b) 'L_AgriOther', includes synthetic fertilisers, animal manures, and organic

Table 1. Soil NO emission factors (EF_{NO}) without background emissions ('NO') and with background emissions ('NO_x-Bg') for synthetic and/or manure N applications for croplands and/or grasslands were calculated from cumulative NO emissions (kg NO-N ha^{-1}) and N application rates (kg N ha^{-1}), using temperate climate data from Liu *et al* [16], and see section 2.1.

	Synthetic and Manure N		Synthetic N		Manure N	
	NO	NO-Bg	NO	NO-Bg	NO	NO-Bg
	Cumulative NO-N emissions as a % of N applied					
Croplands and Grasslands (all data)						
Average	1.40	0.60	1.51	0.49	1.04	1.01
Median	0.40	0.28	0.47	0.35	0.29	0.07
SE[a]	0.26	0.19	0.32	0.08	0.43	0.87
Min[b]	0.00	0.01	0.00	0.01	0.02	0.01
Max[c]	18.74	12.28	18.14	2.58	12.66	12.28
n[d]	129	65	98	51	31	14
Croplands						
Average	1.56	0.55	1.67	0.31	1.19	1.57
Median	0.40	0.15	0.45	0.27	0.29	0.05
SE	0.33	0.28	0.39	0.05	0.57	1.53
Min	0.00	0.01	0.00	0.01	0.02	0.01
Max	18.74	12.28	18.74	1.08	12.66	12.28
n	102	43	79	35	23	8
Grasslands						
Average	0.79	0.71	0.86	0.87	0.62	0.26
Median	0.47	0.47	0.48	0.54	0.29	0.21
SE	0.16	0.15	0.19	0.19	0.28	0.08
Min	0.13	0.03	0.13	0.10	0.17	0.03
Max	2.85	2.58	2.85	2.58	2.53	0.53
n	27	22	19	16	8	6

[a] SE = standard error of the mean.
[b] Min = minimum.
[c] Max = maximum.
[d] *n* = number of observations.

fertilisers applied to soils, crop residues, indirect emissions; but also non-soil related activities, such as off-farm storage, field burning of residues and pesticides. These non-soil related sources are estimated to represent ~3% of total 'L_AgricOther' emissions in Europe. It was not possible to separate these minor sources, as they are reported as a single emission source; (c) the remaining GNFR categories include industrial sources, transport shipping, fugitive emissions and solvents. For simplicity, in this paper these three categories are labelled as (a) 'Manure management', (b) 'N application to soils', and (c) 'Non-agricultural sources'.

Gridded NO_x emission estimates (at a spatial resolution of 0.01 × 0.01 degree), as used in the EMEP model, were downloaded for the years 1990–2017 from the EMEP website and mapped for the European continent. The proportion of emissions associated with agricultural activity were estimated by comparing emissions from manure management and synthetic and organic N application to soils (GNFR K&L) against total gridded emissions. As N application to soils is a key driver of NO_x emissions, country level data of FAO domains 'synthetic fertilisers' and 'manure application to soils' were downloaded from FAOSTAT [27] for the years 2002 and 2017, and linked to European country boundary information for 2016 [28]. European population statistics were downloaded from [29], and areas of agricultural and forest land use were downloaded from FAOSTAT [27].

3. Results

3.1. Soil NO and N_2O emission rates and factors for temperate climate zones

The average rate of synthetic N fertilisers and manures applied to crop and grasslands across 129 studies in temperate climates(140 ± 6.9 kg N ha^{-1}) resulted in average cumulative NO-N and N_2O-N emissions of 1.37 ± 0.34 kg NO-N ha^{-1} and 3.86 ± 0.56 kg N_2O-N ha^{-1}, respectively; and of 0.18 ± 0.06 kg NO-N ha^{-1} and 0.95 ± 0.27 kg N_2O-N ha^{-1}, when background emissions (no N applied) were subtracted [16–23]. Disaggregation to crop and grasslands resulted in 2.6 times larger soil NO emissions from crops than grasslands. The opposite was the case for soil N_2O emissions, with 1.3 times larger N_2O emissions from grasslands (figure 1). The type of synthetic N fertilisers and manures applied to crop and grasslands did not significantly influence soil NO emission rates. However, soil N_2O emissions after manure applications were four times larger from crops, and three times larger from grasslands compared to synthetic N fertilisers (figure 1).

Soil NO EFs were calculated without ('NO') and with background (Bg) emissions ('NO-Bg').

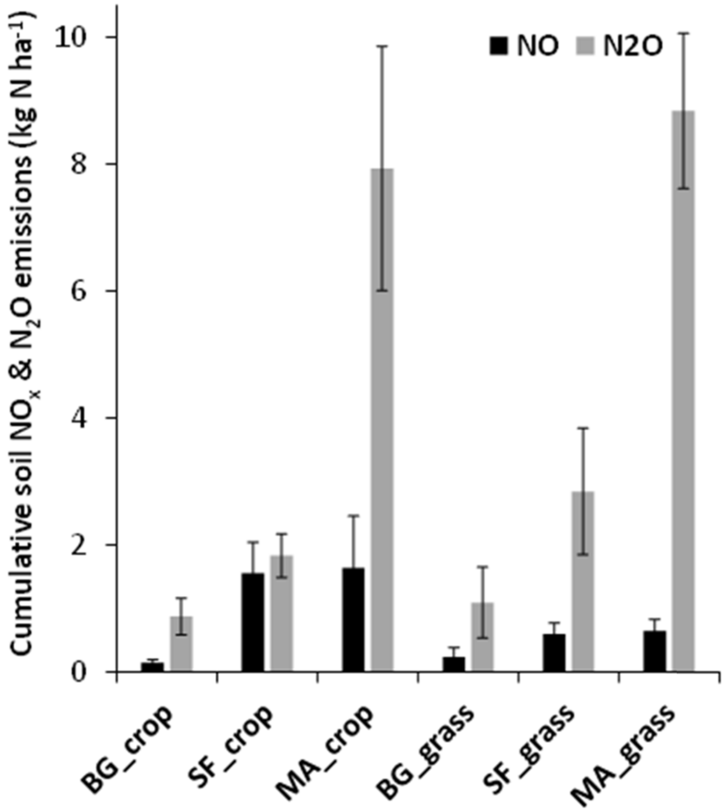

Figure 1. Soil NO and N_2O average emission rates and standard errors from crop and grasslands in temperate climate zones [16–23], and see section 2.1. BG: background emissions, with no fertilisers applied ($n = 17/10$ for crops/grass). SF: synthetic N application to soils ($n = 79/19$ for crops/grass). MA: Manure application ($n = 23/8$ for crops/grass).

Including background emissions reduced the number of data points from 129 to 65 observations for synthetic N and manure N applications, and separately for applications of 'synthetic N' and 'manure N', only (table 1). Subtracting background NO emissions from synthetic and manure N data reduced the EF_{NO} from 1.4% to 0.6% (table 1). Similar reductions were calculated for croplands. This is not surprising as 80% of the data are from fertilised croplands but only 20% from fertilised grasslands. In addition, 76% of the data received synthetic N fertilisers and only 24% received manures. This means the EF analysis is heavily biased towards croplands fertilised with synthetic N compounds. For croplands, EF's without subtracting background emissions (column 'NO'; table 1), (average EF_{NO} 1.56%, range 0.00–18.74, $n = 102$) were twice as large as those from grasslands (average EF_{NO} 0.79%, range 0.13–2.85, $n = 27$). However, such differences were not observed when subtracting the background EF_{NO} from croplands (EF_{NO} 0.55%), and grasslands (EF_{NO} 0.71%) (column 'NO–Bg'; table 1).

Given the small number of data points and large min-max ranges and standard errors (SEs), we do not recommend to use separate EFs for the four individual categories: synthetic N crop/grass and manure N crop/grass (table 1). Instead, with the existing data a single EF for croplands and grasslands combined is the most statistically 'robust' recommendation for N fertiliser and manure induced soil NO emissions in temperate climates of EF_{NO} 1.4%, (0.11%/1.0%, $n = 129$), and soil NO–Bg EF_{NO} 0.6% (0.06%/0.54%, $n = 65$; data are average EF_{NO} and 25th/75th percentiles).

3.2. Relative changes of total and soil NO_x emissions across Europe

Between 1990 and 2017 non-agricultural NO_x sources decreased by 51% in Eastern and 61% in Western Europe. Over this period, agricultural emissions (synthetic and manure N applications) only achieved modest reductions of 7.8% and 19.1% for Eastern and Western Europe, respectively (table 2). The faster decline of non-agricultural sources compared to agricultural sources has led to a consistent increase in the contribution of agricultural NO_x emissions from 3.2% in 1990 to 5.9% in 2017 in Eastern Europe, and from 3.8% in 1990 to 7.4% in 2017 in Western Europe (figure 2).

Total NO_x emission reductions between 1990 and 2017 vary significantly for individual countries, with largest reductions from the Ukraine, UK, and Czech Republic (range 73%–78%), smallest reductions from Cyprus, Norway, Serbia and Poland (range 13%–26%), and increased emissions from Montenegro (83%) and Albania (5%). The eight most populated countries, Poland, Russian Federation,

Table 2. Comparison of NO_x concentrations for agricultural and non-agricultural sources in Eastern and Western European countries.

		Source of NO_x ($Gg\_NO_x\ y^{-1}$)		
	Year	Manure Management[a]	N application to soils[b]	Non-agricultural sources[c]
Eastern European countries	1990	27.8	296.0	9692.6
	2005	13.2	168.7	6188.6
	2017	11.7	286.8	4786.3
Western European countries	1990	20.8	533.5	14406.3
	2005	18.7	427.7	9872.6
	2017	18.3	430.4	5635.1

[a]EMEP categories 'K_AgriLivestock.
[b]'L_AgriOther'.
[c]Non-agricultural sources [26].

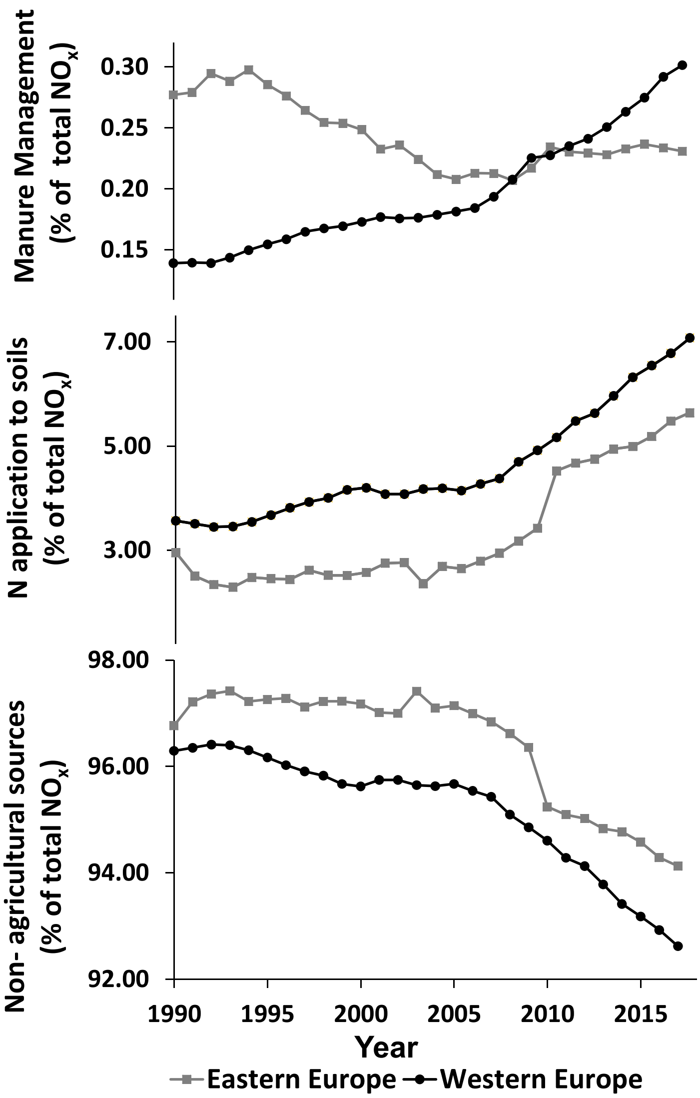

Figure 2. Changes in the contribution of agricultural and non-agricultural sources of NO_x in Eastern and Western European countries for the period 1990–2017 [14].

Ukraine, France, Germany, Italy, Spain and the UK, accounted for 76% of the total population and for 73% of total NO_x emissions of the European continent in 2017. For these eight countries, large reductions of 74% for the non-agricultural sources, with little changes for the category 'N application to soil' (+1.7%) and a 167% rise in livestock-related NO_x emissions has shifted the balance of the dominance of non-agricultural sources in 1990 (84%) to almost equal shares of agricultural (44%) and non-agricultural (56%) emissions in 2017 (table 3). For the remaining 36 European countries, the

Table 3. Comparison of agricultural and non-agricultural NO_x emissions from the 8[a] most populated countries with the remaining 36 countries on the European continent.

	Year		Source of NO_x ($Gg\_NO_x\ y^{-1}$) *fraction of each category (% of total)*		
			Manure management[b]	N application to soils[c]	Non-agricultural sources[d]
All-minus eight countries	1990	Gg	16.3	341.9	6229.8
		%	*0.25*	*5.19*	*94.6*
	2017	Gg	10.9	265.8	2781.0
		%	*0.36*	*8.69*	*91.0*
Eight high population countries	1990	Gg	36.8	3533.3	17 869.1
		%	*0.17*	*16.5*	*83.3*
	2017	Gg	98.4	3592.2	4597.9
		%	*1.19*	*43.3*	*55.5*

[a]Poland, Ukraine, The Russian Federation, Spain, Italy, France, UK, Germany account for 76% of the population on the European continent in 2017 [29].
[b]EMEP categories 'K_AgriLivestock.
[c]'L_AgriOther'.
[d]Non-agricultural sources [26].

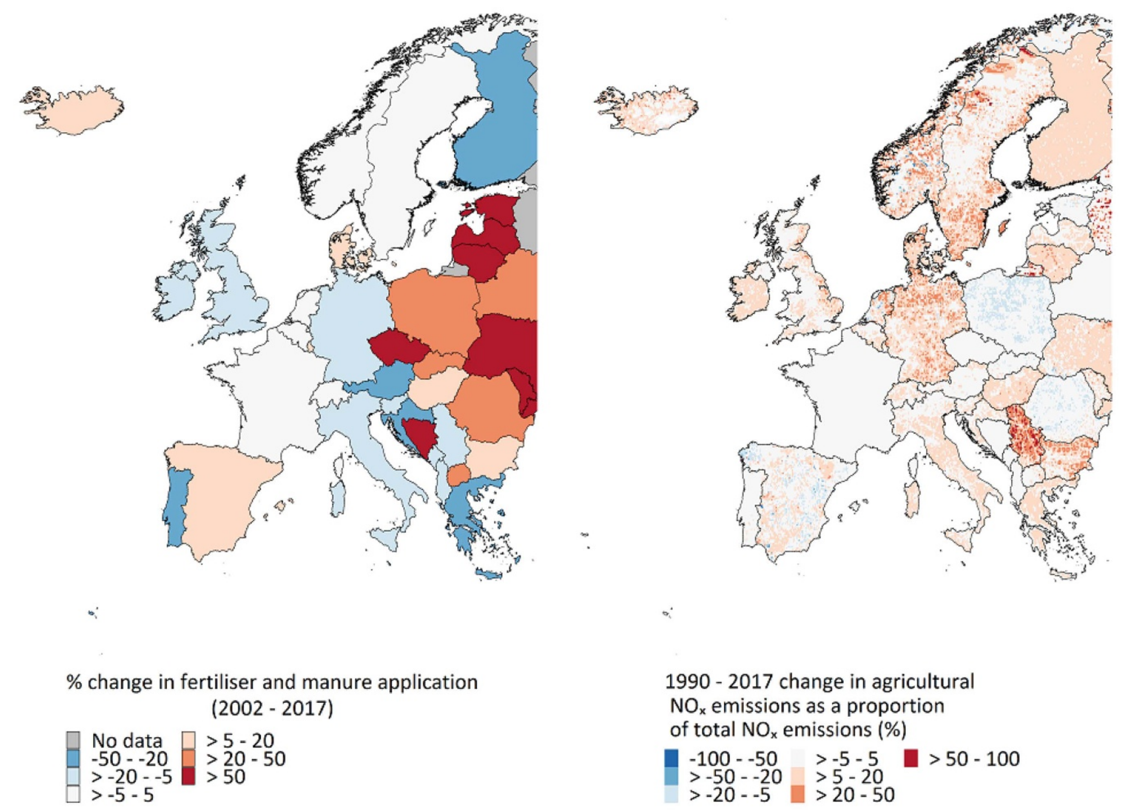

Figure 3. Changes of synthetic N fertiliser and manure application (left map, FAO.FAOSTAT. License: CC BY-NC-SA 3.0 IGO); and agricultural NO_x emissions as a proportion of total NO_x emissions (right map) for 22 Western and 20 Eastern European countries over the period 2002–2017 [14, 26–28].

contribution of the categories 'manure management', 'N application to soil' and 'non-agricultural sources' has hardly changed over the period 1990 and 2017. There is a slight shift from the non-agricultural to the agricultural sources, but insignificant compared to changes observed for the 'eight high population countries'.

An additional source to include in this analysis is soil NO emissions from forests. Median fluxes from 30 forests were 0.43 kg NO-N $ha^{-1}\ y^{-1}$ (range 0–9.3), and converted to NO_2, 1.41 kg $NO_2\ ha^{-1}\ y^{-1}$ [16, 24, 25]. Multiplying this emission rate by forest land areas, suggests that the large areas of Eastern European forests (877 million ha in 2017) emitted 1239 Gg NO_2 in 2017, whereas the much smaller forested areas in West European countries (137 million ha) emitted 194 Gg $NO_2\ y^{-1}$.

4. Discussion

4.1. Soil NO_x emission rates and factors for temperate climate zones

Calculations of soil NO emission rates and fertiliser/manure induced EF's are based on field measurements, which investigate the response of NO-N flux to N fertiliser application rate. Ideally, the duration of these measurements should be for at least one year, to encompass seasonal differences; and even for several years to account for climate extremes. They should be of high frequency, to take into account environmental and agricultural management changes [17, 30] and of high replication rate, due to large spatial and temporal variabilities [17, 31]. They should also include control plots without N application (i.e. background emissions), preferably cover not only cropping seasons but also pre- and post-harvest periods, and account for legacy effects of previous managements (i.e. legumes, crop residues) [17]. Only a few studies have achieved this rigor for soil NO flux measurements [17, 32], compared to large numbers of such studies for N_2O flux measurements [33]. There are two reasons for this discrepancy: (a) the agricultural sector is only a small source of NO (figure 1), but the main source of N_2O [34] and (b) soil NO measurements are rather cumbersome, as the short life-time of NO (30 s) requires immediate analysis with currently rather power-hungry instruments situated in the field [17, 35–37]. In contrast, N_2O is a very stable gas and can be analysed off-line.

Several global meta-analyses have calculated soil EF_{NO}, the most recent ones by Stehfest *et al* [38] and Liu *et al* [16]. The Stehfest analysis is based on 189 measurements published between 1988 and 2004. Liu *et al* [16] extended this data series to 2015, with 520 field measurements. Stehfest *et al* [38] calculated an EF for NO-N of 0.55% of N input with a 95% confidence interval of −80% and +406% for crop and grasslands (excluding legumes). Liu *et al* [16] provided an EF_{NO} of 0.87% (range 0.47–1.27) for grasslands ($n = 32$) and 0.84% (range 0.31–1.37) for croplands ($n = 113$), and an overall global EF_{NO} of 1.14%. The EF_{NO} calculated in this study, using data from temperate climates ($EF_{NO} = 0.60\%$, range 0.01–12.28 from crop and grasslands; table 1) is not dissimilar to Stehfest's and Liu's calculations for global data [16, 38], considering the large uncertainty ranges. However, the EF_{NO} (1.33%), recommended by the EEA [3], is considerably larger than the EF_{NO} calculated in this study. The EEA EF_{NO} (1.33%) calculation is also based on Stehfest's compilation of global data [38], but only includes data from North America, Europe and the former USSR. For EEA inventory reporting NO emission rates and EF_{NO} are required to be converted to NO_2 in order to compare the soil NO-N emissions with combustion sources (NO_x). The EF_{NO} 1.33% translates to EF_{NO2} 4.14% (0.04 kg NO_2/kg N applied, with 95% confidence intervals of 0.005–0.104 soil NO_2 emissions) [3].

The large uncertainty ranges for all four EF_{NO} calculations (Liu, Stehfest, EEA and this study) imply that respective EF_{NO} values (∼0.87% [3], 0.55% [38], 1.33% [3], 0.60% this study) are probably not very different. We therefore decided to use the EEA EF_{NO} to calculate the NO emission rates presented in figures 2 and 3 and tables 2 and 3.

Out of the 43 publications included in our EF_{NO} analysis [16, 18–23], only 19 studies are post 2004. This is rather concerning, and points to the need of many more field based soil NO measurements across the European climate zones and their main agricultural management practices (crop categories, fertiliser practices, tillage, irrigation, and manure management).

Manure management EF's (reported as NO_2) were recently updated for the national reporting framework (NRF) source categories, and range from 0.0001 (laying hens: slurry) to 0.752 (dairy cattle: solids) [39]. As for soil NO emissions, these values also are highly uncertain due to lack of data. The contribution of manure management to total European NO_x emissions is 0.23% in Eastern Europe and 0.30% in Western Europe in 2017 compared to 5.6% and 7.1% from synthetic and manure N applied to soils for Eastern and Western Europe, respectively (figure 2). However, per area basis manure stores are small compared to fields, but they provide concentrated hotspots of NO_x, not to be ignored.

Tier 2 NO EFs, based on, i.e. different agricultural and manure management practices, fertiliser regimes, crop and soil categories, are not available, due to the lack of sufficient data [3]. However, Tier 3 process-based modelling, using the denitrification decomposition model (DNDC), was developed to calculate soil NO_x emissions from not only agricultural soils but also from forest soils (e.g. [40–42]). For the EU15 countries in the year 2007, emissions from N fertilised soils were 332 Gg NO_x y^{-1} [5], and are in agreement with the EMEP Tier 1 approach (306 Gg NO_x y^{-1}). Considering the large uncertainties of such estimates provides some level of confidence in the EMEP EEA Tier 1 approach. One must not forget that forests are important sources of soil NO_x emissions, especially in areas with large atmospheric N deposition rates. Forests are efficient traps for pollutants, with N deposition rates much larger than to short vegetation [43]. In addition the typical low forest soil bulk densities favour NO production [16, 25, 40, 44]. At the global scale forest soil NO_x emission rates (2.7 kg NO-N ha^{-1} y^{-1}) are of the same order of magnitude as fertilised crops and grasslands (2.8 and 2.4 kg NO-N ha^{-1} y^{-1}) [16]. Similarly, for the EU15 agricultural emissions were only 1.3 times larger than forest emissions [5]. Pledges and policies of increased tree planting in Europe as a panacea to combat climate change may increase soil NO_x emission from forests.

4.2. Relative changes in total and soil NO_x emissions across Europe

On average, non-agricultural NO_x emissions have decreased between 1990 and 2017 from the 42 countries of the European continent by 56%.

(figure 2, table 1), and are highly likely to decline further through developments of green transport policies and further industrial reductions [45, 46]. Agricultural sources of NO_x also declined, albeit at modest rates. For Western Europe, the reduction in 'N applied to soil' coincided with a 4% reduction in N fertiliser application. In contrast, N fertiliser use increased by 57% in Eastern Europe (figure 3, table 2), with little change in soil NO_x emissions between 1990 and 2017.

This study has provided an overview of changes in agricultural NO_x emissions in response to N fertilisation and manure management within the context of total NO_x emissions and focus on the collective Eastern versus Western European countries. There is large variability in the percentage contribution of agricultural soil NO_x emissions to total emissions for individual countries (figure 3). For example, country level disaggregation of the change in N fertiliser application does not directly match the changes in agricultural NO_x emissions as a proportion of total NO_x emissions, because of a range of drivers; mainly land management, population densities and industrialisation (figure 3).

The downward trend of overall NO_x emissions is encouraging, but the increased contribution from agricultural and forest soils and manure management is of concern, for several reasons. (a) Uncertainties of the soil and manure management related emissions are too large to provide accurate predictions of high O_3 events. Especially biogenic NO_x emissions from N applications to soils, manure management and forests can be important sources of European atmospheric O_3 concentrations, particularly in spring (N fertilisation period) and summer periods (dry soils, which promote NO over N_2O production) [47, 48]. (b) Climate change predictions of reduced rainfall and increased drought events across many parts of Europe will favour soil NO_x over soil N_2O emissions from N fertilised soils, because dry and well aerated soils provide the O_2 required for microbial NO production, whereas low O_2 concentrations are needed for N_2O production [6, 8]. (c) Increased tree planting may increase soil NO_x emissions unless atmospheric N deposition rates arising from agricultural reactive N emissions (mainly ammonia) and fossil fuel combustion sources are declining. A potential NO_x mitigation option would be to lime forest soils, but this could increase N_2O emissions and NO_3 leaching, which needs to be studied prior lime application to avoid pollution swapping [49].

5. Conclusions

NO_x emission rates from N fertilised soils, manure management practices and forest soils are highly uncertain, because of the lack of good quality datasets. Randomised plot experiments with high spatial and temporal resolution, including a background control across the European climate zones, main crop types and key agricultural management practice are essential to improve modelling of soil NO_x emissions and develop mitigation options, and thereby improve the predictions of atmospheric O_3 production. This knowledge gap in soil NO_x emissions could be solved, if long-term monitoring networks, such as ICOS (Integrated Carbon Observation System) and eLTER (i.e. European Long-Term Ecosystem Research Infrastructures), would include soil and canopy NO_x emissions as mandatory measurements for fertilised croplands, grasslands and forests.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Ethical statement

There are no ethical concerns regarding this data analysis.

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References

[1] IPCC 2006 *2006 IPCC guidelines for national greenhouse gas inventories* vol 4 *Agriculture, Forestry and Other Land Use* (available at: www.ipccnggip.iges.or.jp/public/2006gl/pdf/4_Volume4/V4_05_Ch5_Cropland.pdf)
[2] IPCC 2019 *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Box 4.3A. 2019* (available at: www.ipcc.ch/report2019-refinement-to-the-2006-ipcc-guidelines-for-national-greenhouse-gas-inventories)

[3] Hutchings N, Webb J and Amon B 2016 *3.D Crop Production and Agricultural Soils* (available at: www.eea.europa.eu/publications/emep-eea-guidebook-2019/part-b-sectoral-guidance-chapters/4-agriculture/3-d-crop-production-and/view)
[4] Butterbach-Bahl K, Stange F, Papen H and Li C 2001 Regional inventory of nitric oxide and nitrous oxide emissions for forest soils of southeast Germany using the biogeochemical model PnET-N-DNDC *J. Geophys. Res. Atmos.* **106** 34155–66
[5] Butterbach-Bahl K, Kahl M, Mykhayliv L, Werner C, Kiese R and Li C 2009 A European-wide inventory of soil NO emissions using the biogeochemical models DNDC/Forest-DNDC *Atmos. Environ.* **43** 1392–402
[6] Medinets S, Skiba U, Rennenberg H and Butterbach-Bahl K 2015 A review of soil NO transformation: associated processes and possible physiological significance on organisms *Soil Biol. Biochem.* **80** 92–117
[7] Feng Z, De Marco A, Anav A, Gualtieri M, Sicard P, Tian H, Fornasier F, Tao F, Guo A and Paoletti E 2019 Economic losses due to ozone impacts on human health, forest productivity and crop yield across China *Environ. Int.* **131** 104966
[8] Butterbach-Bahl K, Baggs E M, Dannenmann M, Kiese R and Zechmeister-Boltenstern S 2013 Nitrous oxide emissions from soils: how well do we understand the processes and their controls? *Phil. Trans. R. Soc.* B **368** 20130122
[9] Heil J, Vereecken H and Brüggemann N 2016 A review of chemical reactions of nitrification intermediates and their role in nitrogen cycling and nitrogen trace gas formation in soil *Eur. J. Soil Sci.* **67** 23–39
[10] Skiba U, Hargreaves K J, Fowler D and Smith K A 1992 Fluxes of nitric and nitrous oxides from agricultural soils in a cool temperate climate *Atmos. Environ.* **26** 2477–88
[11] Skiba U and Ball B 2002 The effect of soil texture and soil drainage on emissions of nitric oxide and nitrous oxide *Soil Use Manag.* **18** 56–60
[12] Maljanen M, Martikkala M, Koponen H T, Virkajärvi P and Martikainen P J 2007 Fluxes of nitrous oxide and nitric oxide from experimental excreta patches in boreal agricultural soil *Soil Biol. Biochem.* **39** 914–20
[13] Barrón V *et al* 2020 Photochemical emission and fixation of NOx gases in soils *Sci. Total Environ.* **702** 134982
[14] EEA 2017 *Annual European Union (EU) LRTAP Convention Emission Inventory Report 1990–2017* (available at: www.eea.europa.eu/publications/european-union-emissions-inventory-report-2017) (Accessed: July 2020)
[15] Almaraz M, Bai E, Wang C, Trousdell J, Conley S, Faloona I and Houlton B Z 2018 Agriculture is a major source of NOx pollution in California *Sci. Adv.* **4** 1–8
[16] Liu S, Lin F, Wu S, Ji C, Sun Y, Jin Y, Li S, Li Z and Zou J 2017 A meta-analysis of fertilizer-induced soil NO and combined NO+N2O emissions *Glob. Change Biol.* **23** 2520–32
[17] Medinets S, Gasche R, Skiba U, Medinets V and Butterbach-Bahl K 2016 The impact of management and climate on soil nitric oxide fluxes from arable land in the Southern Ukraine *Atmos. Environ.* **137** 113–26
[18] Shepherd M F, Barzetti S and Hastie D R 1991 The production of atmospheric NOx and N_2O from a fertilized agricultural soil *Atmos. Environ.* **25** 1961–9
[19] Slemr F and Seiler W 1984 Field measurements of NO and NO_2 emissions from fertilized and unfertilized soils *J. Atmos. Chem.* **2** 1–24
[20] Slemr F and Seiler W 1991 Field study of environmental variables controlling the NO emissions from soil and the NO compensation point *J. Geophys. Res.* **96** 13017–31
[21] Valente R J and Thornton F C 1993 Emissions of NO from soil at a rural site in Central Tennessee *J. Geophys. Res.* **98** 16,745–16,753
[22] Thornton F C, Bock B R and Tyler D D 1995 Soil emissions of NO and N_2O from injected anhydrous ammonium and urea *J. Environ. Qual.* **25** 1378–84
[23] Williams E J, Parrish D D, Buhr M P, Fehsenfeld F C and Fall R 1988 Measurement of soil NO(x) emissions in central Pennsylvania *J. Geophys. Res.* **93** 9539–46
[24] Remy E, Gasche R, Kiese R, Wuyts K, Verheyen K and Boeckx P 2017 Edge effects on N_2O, NO and CH_4 fluxes in two temperate forests *Sci. Total Environ.* **575** 1150–5
[25] Pilegaard K *et al* 2006 Factors controlling regional differences in forest soil emission of nitrogen oxides (NO and N_2O) *Biogeosciences* **3** 651–61
[26] EMEP Centre on Emission Inventories and Projections (available at: www.eea.europa.eu/publications/emep-eea-guidebook-2013/part-a-general-guidance-chapters/7-spatial-mapping-of-emissions) (Accessed: July 2020)
[27] FAOSTAT Land use (fertilisers by nutrients, forest & agricultural land) (available at: http://faostat.fao.org) (Accessed: July and November 2020)
[28] GISCO: Geographical Information and Maps (available at: https://ec.europa.eu/eurostat/web/gisco/geodata/reference-data/administrative-units-statistical-units/countries) (Accessed: July 2020)
[29] Eurostat: European Population Statistics (available at: https://ec.europa.eu/eurostat/web/population-demography-migration-projections/data/database) (Accessed: July 2020)
[30] Parkin T B and Venterea R T 2010 USDA-ARS GRACEnet project protocols, chapter 3. Chamber-based trace gas flux measurements (Beltsville, MD: Sampling protocols) pp 1e39 (available at: www.ars.usda.gov/ARSUserFiles/31831/2011%20Parkin%20and%20Venterea%20Trace%20Gas%20Protocol%20Revision%20Final.pdf) (Accessed: July 2020)
[31] Ludwig J, Meixner F X, Vogel B and Forstner J 2001 Soil-air exchange of nitric oxide: an overview of processes, environmental factors, and modeling studies *Biogeochemistry* **52** 225–57
[32] Laville P, Lehuger S, Loubet B, Chaumartin F and Cellier P 2011 Effect of management, climate and soil conditions on N_2O and NO emissions from an arable crop rotation using high temporal resolution measurements *Agric. For. Meteorol.* **151** 228–40
[33] Cardenas L M *et al* 2019 Nitrogen use efficiency and nitrous oxide emissions from five UK fertilised grasslands *Sci. Total Environ.* **661** 696–710
[34] Skiba U *et al* 2012 UK emissions of the greenhouse gas nitrous oxide *Phil. Trans. R. Soc.* B **367** 1175–85
[35] Guardia G, Cangani M T, Sanz-Cobena A, Junior J L and Vallejo A 2017 Management of pig manure to mitigate NO and yield-scaled N_2O emissions in an irrigated Mediterranean crop *Agric. Ecosyst. Environ.* **238** 55–66
[36] Abalos D, Sanchez-Martin L, Garcia-Torres L, van Groenigen J W and Vallejo A 2014 Management of irrigation frequency and nitrogen fertilization to mitigate GHG and NO emissions from drip-fertigated crops *Sci. Total Environ.* **490** 880–8
[37] Butterbach-Bahl K, Gasche R, Breuer L and Papen H 1997 Fluxes of NO and N_2O from temperate forest soils: impact of forest type, N deposition and of liming on the NO and N_2O emissions *Nutr. Cycling Agroecosyst.* **48** 79–90
[38] Stehfest E and Bouwman L 2006 N_2O and NO emission from agricultural fields and soils under natural vegetation: summarizing available measurement data and modeling of global annual emissions *Nutr. Cycling Agroecosyst.* **74** 207–28
[39] Amon B, Hutchings N, Dammgen U and Webb J 2016 *3.B Manure Management* (available at: www.eea.europa.eu/publications/emep-eea-guidebook-2019/part-b-sectoral-guidance-chapters/4-agriculture/3-b-manure-management) (Accessed: July 2020)
[40] Medinets S, Gasche R, Skiba U, Schindlbacher A, Kiese R and Butterbach-Bahl K 2016 Cold season soil NO fluxes from a temperate forest: drivers and contribution to annual budgets *Environ. Res. Lett.* **11** 114012

[41] Molina-Herrera S *et al* 2017 Importance of soil NO emissions for the total atmospheric NOx budget of Saxony, Germany *Atmos. Environ.* **152** 61–76

[42] Kesik M *et al* 2005 Inventories of N_2O and NO emissions from European forest soils *Biogeosciences* **2** 353–75

[43] Fowler D, Cape J N, Coyle M, Flechard C, Kuylenstierna J, Hicks K, Derwent D, Johnson C and Stevenson D 1999 The global exposure of forests to air pollutants *Water Air Soil Pollut.* **116** 5–32

[44] Medinets S, Gasche R, Kiese R, Rennenberg H and Butterbach-Bahl K 2019 Seasonal dynamics and profiles of soil NO concentrations in a temperate forest *Plant Soil* **445** 335–48

[45] Monforti-Ferrario F, Astorga-Llorens C and Pisoni E 2019 *Policy Pressures on Air—Anticipating Unforeseen Effects of EU Policies on Air Quality, EUR 29974 EN* (Luxembourg: Publications Office of the European Union) (https://doi.org/10.2760/566649)

[46] Vleugel J M and Bal F 2019 Towards zero CO_2−, NO_x− and PM_{10}- emissions by passenger cars: technology & behaviour *Int. J. Environ. Impacts* **2** 192–205

[47] Visser A J, Boersma K F, Ganzefeld L N and Krol M C 2019 European NO_x emissions in WRF-Chem derived from OMI: impacts on summertime surface ozone *Atmos. Chem. Phys.* **19** 11821–41

[48] Vuolo R M, Loubet B, Mascher N, Gueudet J-C, Durand B, Laville P, Zurfluh O, Ciuraru R, Stella P and Trebs I 2017 Nitrogen oxides and ozone fluxes from an oilseed-rape management cycle: the influence of cattle slurry application *Biogeosceinces* **14** 2225–44

[49] Butterbach-Bahl K, Gasche R, Willibald G and Papen H 2002 Exchange of N-gases at the Höglwald Forest—a summary *Plant Soil* **240** 117–23