Review Articles

Greenhouse Effect of NO_X

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Abstract

Through various processes the nitrogen oxides (NO_x) interact with trace gases in the troposphere and stratosphere which do absorb in the spectral range relevant to the greenhouse effect (infrared wavelengths). The net effect is an enhancement of the greenhouse effect. The catalytic role of NO_x in the production of tropospheric ozone provides the most prominent contribution. The global warming potential is estimated as GWP (NO_x) = 30 – 33 and 7 – 10 for the respective time horizons of 20 and 100 years, and is thereby comparable to that of methane. NO_x emissions in rural areas of anthropogenically influenced regions, or those in the vicinity of the tropopause caused by air traffic, cause the greenhouse effectivity to be substantially more intense. We estimate an additional 5 – 23 % for Germany's contribution to the anthropogenic greenhouse effect as a result of the indirect greenhouse effects stemming from NO_x. Furthermore, a small and still inaccurately defined amount of the deposited NO_x which has primarily been converted into nitrates is

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again released from the soil into the atmosphere in the form of the long-lived greenhouse gas nitrous oxide (N_2O). Thus, anthropogenically induced NO_x emissions contribute to enhanced greenhouse effect and to stratospheric ozone depletion in the time scale of more than a century.

Key words: Nitrogen oxides; greenhouse effect; greenhouse gases; trace gases ozone; formation; ozone depletion; troposphere; stratosphere; atmosphere; chemical reactions

1 Sources

Nitrogen oxides (NO_x = NO + NO_2) are primarily emitted in the form of NO. Through the reaction with ozone on the one hand and through the photolysis of NO_2 on the other, a photochemical equilibrium is achieved very rapidly in the atmosphere (i.e. in a matter of minutes). Oxidative processes convert these substances almost completely into nitric acid or nitrates, and these products are again removed from the atmosphere via dry or wet deposition within only a few days. For this reason, and because of the great diversity of mobile and stationary sources, their distribution is heterogeneous both spatially and temporally, and primarily limited to regions in the vicinity of these sources. A small proportion of the nitric oxides is also transported greater distances in the form of reservoir compounds (peroxynitric acid, $HOONO_2$, and peroxyacyl nitrates, $RC(O)OONO_2$ (R = alkyl, e.g. CH_3)). It is difficult to reliably quantify the various sources because of the complex interdependencies of parameters seen in the number of varying location (LOGAN 1983; PENNER et al. 1991). This is especially the case for the non-industrial regions where sources which are difficult to characterize predominate (uncertainty factor of approximately 2) like thunderstorms, biomass burning and exhalations from the soil (as a result of microbial activity). The most important anthropogenic source is the combustion of fossil fuels (uncertainty of approximately ± 30 %) in the sectors of transportation and energy supply, while the agriculture and biomass burning plays a lesser role. In spite of the only slight increases or even stagnation in the regions of the largest sources, i. e. North America and Europe, the emissions nevertheless continue to increase globally (HAMEED and DIGNON 1991). The distribution of the most important sources are seen in **Table 1**.

Table 1: Mean emission flux of NO_x and sectorial distribution in 1992 (EHHALT and DRUMMOND 1982; LOGAN 1983; Umweltbundesamt 1992)

	Globally	Germany
All sources (10^{12}g NO_x-N year^{-1}	48.5 (25 – 60)	1.35
Individual sectors (% as NO_2)		
Combustion of fossil fuels:	40 (28 – 56)	93
for the production of energy and heat, industry		27(a)
for transportation		66(a)
for air traffic	1.2	
Agriculture and biomass burning	25 (16 – 28)	<3
Natural sources (b)	35 (7 – 47)	<1

(a) West Germany 1989

(b) soils (microbial activity), thunderstorms, oceans, effects from the stratosphere, oxidation of ammonia)

2 Greenhouse Effect

The atmospheric chemistry of the nitrogen oxides has indirect consequences on the radiative forcing while, the direct greenhouse effect through the absorption of longwave radiation of trace gases NO and NO_2 is negligible.

The potential greenhouse effect of the trace gases, quantified as the GWP[1], provide an estimate of the relative effectiveness of trace gases in a defined time horizon. These determinations permit a fairly reliable estimation for the long-lived trace gases, i.e. such gases as are well mixed in the troposphere as long as the composition of the atmosphere does not change dramatically. The spatial and temporal distributions of short-lived trace gases are highly heterogeneous leading to regional and temporal variability in related GWPs. If short-lived trace gases influence the concentration of long-lived greenhouse gases, these do not generally demonstrate linear dependency because of complex chemical mechanisms including higher order kinetics and feedbacks (LIU et al. 1987; LIN et al. 1988; MOUSSIOPOULOS 1990; etc.). Thus, the global GWP of short-lived trace gases through direct radiative forcing and, even more, through indirect radiative forcing as resulting from chemical reactivity can only be estimated with considerable uncertainty.

2.1 First Order Indirect Greenhouse Effect – Production of Tropospheric Ozone

Depending on the concentration of the NO_x level, there is either a formation or loss of ozone (O_3) in the troposphere: If the NO_x exceeds a particular threshold value, ozone is formed, while below this level it is removed. The influence of NO_x on the rate of ozone formation is dependent on the site, the altitude and the season of the year. The threshold value is around 10 with a maximum of 30 pptv[2]. An increase in the NO_x concentrations in regions of the troposphere which are low in nitrogen oxides (primarily the regions in the tropics) can result in an alteration from a net O_3 loss to a net O_3 production. In regions of the troposphere which are rich in nitrogen oxides, additional introduction of NO_x causes the ozone concentration to become even higher.

A comparison of the anthropogenically influenced and preindustrial atmospheres has shown that the ozone level near the ground and the total column density of ozone in the troposphere of the northern hemisphere has almost doubled (in Europe from approximately 15 – 20 ppbv in July to 30 – 40 ppbv) while the increase in the southern hemisphere

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[1] Global warming potential. The relative GWP signifies the cumulative radiative forcing relative to emission of the same mass of CO_2 within defined time horizons (IPCC 1990 and 1992)

[2] volume mixing rations:
pptv = parts per trillion by volume = 10^{-12}
ppbv = parts per billion by volume = 10^{-9}

was less pronounced. (CRUTZEN and ZIMMERMANN 1991; HAUGLUSTAINE et al. 1994) These results agree with observations of ozone made in Europe (ATTMANNSPACHER et al. 1984; VOLZ and KLEY 1988). This effect is almost exclusively due to NO_x emissions.

A molecule of NO_2 formed near the ground in a rural, anthropogenically influenced region of the northern hemisphere leads to the production of up to 12 molecules of O_3 (experimental findings by LUKE et al. 1992; GEISS and VOLZ-THOMAS 1993; TRAINER et al. 1993; KLEINMAN et al. 1994; OLSZYNA et al. 1994). In Europe, approximately 3 – 5 can be assumed while a global mean of only about 0.36 molecules of O_3 has been estimated (model calculations by JOHNSON et al. 1992; DERWENT and DAVIES 1994). The broad range of ozone formation efficiency is primarily the result of complex chemical interactions of varying mixtures of reactants. The ozone formation is NO_x limited in rural areas, whereas it is usually limited by the concentration of hydrocarbons in urban areas. Based upon calculations, NO_x emitted on the ground is attributed as having a greenhouse effect (GWP) which is presently estimated as being 30 and 7 during the time horizon of 20 or 100 years, respectively (global mean refering to NO_2 as IPCC, 1990; JOHNSON et al. 1992). The accuracy of the model calculations is dependent on the accuracy of representation of the chemical and radiation processes and has been estimated to be 50 %. For emissions in Germany up to 8 molecules of O_3, by average 4, were observed (Schauinsland/Black Forest, relatively fresh polluted air masses during the summer months of 1989 and 1990; GEISS and VOLZ-THOMAS 1993). This agrees well with model predictions of ozone formation in European countries (DERWENT and DAVIES 1994). In order to estimate a representative efficiency of ozone formation, it must be taken into account that the rate of ozone formation is lower in the winter, that not all NO_x molecules react (dry deposition) and that only small amounts of ozone are formed or lost in the vicinity of NO_x and hydrocarbon sources. On the other hand, somewhat older air masses, i.e. at larger distance from the sources, result in higher turnover rates. Based on the typical seasonal variability of near-ground tropospheric O_3 in Germany, and on the spatial distribution of the NO_x and hydrocarbon sources, we estimate 1.5 molecules of ozone per NO_x in the rural areas and 0.7 – 3 molecules of O_3/NO_x for Germany as a whole (a value which is a factor of 2 – 8 times higher than the global value mentined above). The influence of the NO_x emissions on the ozone formation is also higher at great altitudes in the atmosphere (lower background concentrations and longer residence times of the trace gases). In this way, the same amount emitted from air traffic has an approximately 30 times stronger effect than that emitted on the ground (JOHNSON et al. 1992). During the last decade, air traffic has increased by 5 – 7 %/year worldwide and will probably continue to increase further (ICAO 1992a, 1992b).

2.2 Processes of Higher Order Indirect Greenhouse Effects

2.2.1 NO_x and Methane

Besides other trace species, NO_x also controls the atmospheric concentration of the hydroxyl radical. This is the most important species of tropospheric chemistry as it mediates the removal of most trace substances including that of methane (CH_4).

Based on the dramatic changes in atmospheric trace constituents composition resulting from anthropogenic activities and the especially intensive reactivity of the hydroxyl radical (and the consequent dependence on the concentration of many reaction partners), it can be stated with certainty that its distribution in the troposphere has changed since the pre-industrial era. At least as a rough estimate, these changes can be attributed mostly to NO_x. Increases are partially seen in anthropogenically, influenced regions of the middle latitudes of the northern hemisphere, while decreases are expected in remote areas (CRUTZEN and ZIMMERMANN 1991; THOMPSON 1992; HAUGLUSTAINE et al. 1994). In fact, regions of the troposphere with high OH concentrations tend to prevail in remote areas of the globe, so that for the global average a trend to decreasing OH concentrations can be assumed. With respect to CH_4 this would imply a longer residence time since the global distribution of this trace gas between the zones of increased and decreased OH concentrations is seen to demonstrate a preference in favor of those zones with decreased concentrations. Conservatively, estimate that the CH_4 residence time (global mean) was not increased more than 40 % due to the introduction of antropogenic NO_x (HAUGLUSTAINE et al. 1994). However, since this effect is seen to be a result of the entire anthropogenic NO_x (presently about 1.6×10^{12} g NO_x-N), this indirect greenhouse effect of NO_x can be judged negligible in comparison to others discussed her (GWP (CH_4) < 90; IPCC 1990; BRÜHL 1993).

2.2.2 Production of Nitrous Oxide

Nitrogen oxides are converted to nitric acid and particulate nitrate (aerosol) in the atmosphere. For the most part, this occurs within only a few days. The total flux amounts to $(1.8 \pm 0.1) \times 10^{14}$ g N/year[3]. Soils which are subject to nitrate deposition, emit N_2O as a byproduct of denitrification, which has a long atmospheric residence time and is recognized as a strong greenhouse gas. An estimation of the respective N_2O source is uncertain because of the multitude of site-specific influential factors and other N_2O sources in the soil (nitrification; WILLIAMS et al. 1992). Based upon the knowledge attained from the nitrogenous fertilization of farmland, grasslands and tropical forests, a range of approximately 0.4 – 4 mg N_2O-N emissions/g NO_3^--N can be assumed (BOLLE et al. 1986; KELLER et al. 1988; EICHNER 1990). The amount of 0.26 – 6.5 kg N_2O-N/ha/year which was measured in German deciduous forests and corresponds to approximately 1 – 16 % of NO_3^--N, is certainly influenced by large depositional fluxes of ammonia, nitrates and nitric acid (SCHMIDT et al. 1988; BRUMME and BEESE 1992). So far such studies are sparse and cannot be generalized. In addition, it is not possible to attribute the effect of the input of oxidated nitrogen compounds (as differentiated from that of ammonia). **Table 2** demonstrates that the source strength of the greenhouse gas N_2O is

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[3] An additional quantity of 6×10^{13} g N/year is presently spread in agricultural areas in the form of fertilizer (HAUCK, 1988).

Table 2: Estimation of the N_2O emissions from soil subsequent to NO_x emissions and the corresponding radiative forcing

	Globally	Germany
NO_x-related N quantities (10^{12} g NO_3^--N/year)	48.5 (25 – 60)	1.35
NO_x-related N_2O sources⁽¹⁾ (10^{12} g NO_2-N/year)	0.01 – 0.24	0.0005 – 0.005
All N_2O sources (10^{12} g NO_2-N/year)	5.5 – 16.8⁽²⁾	0.14⁽³⁾

(1) Conservative calculation
(2) IPCC 1992; DASCH 1992; KHALIL and RASMUSSEN 1992
(3) 1990 (Umweltbundesamt 1993)

Emission factor N_2O = 0.4 – 4 mg N_2O-N emission/g NO_3-N quantity
Stoichiometric factor NO_3/NO_x = 1
GWP = 290 (over a temporal horizon of 20 years) GWP = 320 (over a temporal horizon of 100 years; IPCC 1994; where GWP = a measurement for the greenhouse effectivity relative to an equal mass of CO_2)
NO_2-related greenhouse potential = 0.38 – 3.8 (temporal horizon of 20 years), 0.41 – 4.1 (temporal horizon of 100 years)

increased by the emission of NO_x and that this increase is a matter of a few percent both globally and in Germany. This adds globally to 0.2×10^{12} g N_2O-N/year or 1.2 – 3.6 % at present (DASCH 1992).

Effect of N_2O in the Stratosphere . . .

N_2O has an atmospheric residence time[4] of approximately 120 years, whereby its oxidation in the stratosphere represents the only substantial sink.

$10 \pm 3 \times 10^{12}$ g N_2O-N are introduced into the stratosphere per year (CRUTZEN 1978). Since it is the precursor of NO, N_2O is the most prominent reagent of the various ozone decay reactions in the stratosphere. 31 % of the ozone present are removed through this path (global and vertical mean; in fact, this reaction is only active above ca. 24 km of altitude; CRUTZEN 1983; CRUTZEN and SCHMAILZL 1983). Thus, the use of mineral fertilizers in agriculture contributes to the destruction of the stratospheric ozone layer. Determined globally, the ozone in the atmosphere decreases currently by approximately – 0.25 %/year (– 0.45 %/year in 40° – 50° N latitudes reference periods 1979 – 1994; WMO 1995).

Based upon model calculations, an increase in the tropospheric N_2O concentration of about 100 % is related to a decrease in the ozone content of the stratosphere of approximately 12 % (CRUTZEN 1983), whereas an increase in N_2O of about 20 % results in a reduction of the total ozone of about 4 % (NRC 1984).

An upper limit for the greenhouse effectivity can be estimated as follows: The admixture of 1 kg of N_2O results in the destruction of 0.73 kg of O_3 (+ 20 % N_2O or 62 ppbv N_2O = 0.70 g/m² N_2O total column density over a column height of 10 km and a mean pressure of 550 hPa, O_3 total column density < 300 Dobson units or 6.4 g/m², molar masses N_2O/O_3 = 0.96), which is equivalent to a N_2O-related GWP < 1460 (with a GWP (O_3) < 2000 with a maximum in the lower stratosphere where no N_2O-related ozone depretion occurs) and an NO_x-related GWP < 0.6 (emission factor 0.4 mg N_2O-N/g NO_x-N). After 20 years, approximately three-quarters of 14 %, and after 100 years of 54 % of the emitted N_2O have reached the stratosphere, a quantity which corresponds to upper limits of the GWP during these time horizons of 0.05 or 0.24, respectively.

. . . and consequences for the Troposphere

The tropospheric photochemistry is intensified by a decrease of stratospheric ozone. The photolysis rate of ozone in the troposphere, for example, which regulates the formation of hydroxyl radicals, increased globally by an average of 6.3 % between 1970 and 1990 (FUGLESTVEDT et al. 1994). This corresponds with an increase in the concentration of OH radicals and a reduction in the residence time of most trace substances including that of methane, the elimination of which is alone dependent on the hydroxyl radical. Depletion of stratospheric ozone is primarily a result of the elevated concentration of chlorine in the stratosphere. Nevertheless, as estimated above, the emission of NO_x also indirectly leads to the destruction of ozone via the additional formation of N_2O. This occurs at a rate of approximately 0.3 g O_3/kg NO_x.

The rate of depletion of the total O_3 column during the period 1970 – 1990 was approximately 4.5 % or 0.28 g O_3/m² = 1.4. 10^8 to 0_3 (earth's surface = 5. 10^{14} m²). This corresponds to a reduction of the tropospheric residence time of methane of about 5. 10^{-11} % per kg of O_3 (refering to global means). Since the residence time demonstrates a linear relationship to the greenhouse warming potential of CH_4, and this is not very high (GWP (CH_4) < 90; IPCC; BRÜHL, 1993), this indirect influence of NO_x can be neglected.

2.2.3 Effects on the Photochemical Aerosol Formation

Natural and anthropogenic trace gases undergo oxidative processes which result in the formation of less volatile and finally of condensable compounds. In this regard, the most important process is the oxidation of SO_2 to sulfuric acid. SO_2 is emitted directly (primarily anthropogenically) and – of equal significance on the global scale – also formed in atmospheric chemistry from natural precursors (dimethyl sulfide). Airborne particles are thereby formed from gaseous precursors and cloud condensation nuclei are consequently made available. The radiation effective characteristics of these processes lead to a clear cooling (negative radiative forcing) as a result of the increased reflectivity of the particles and the cloud drops (so-called direct and indirect aerosol effects, together approximately – 0.9 ± 0.6 W/m² for the anthropogenic portion; CHARLSON et al. 1992; KIEHL and BRIEGLEB 1993).

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[4] The residence time is defined as the period until the concentration has declined to 37 % (1/e) of its initial value.

In cloud-free regions of the atmosphere, the reaction of the hydroxyl radical governs the rate of SO_2 oxidation and thus aerosol formation. In NO_x-burdened air, the hydroxyl radical is found at higher concentrations due to the more efficient recycling mechanisms. Regarding the dispersion of emissions, it can be seen that the more rapid the process of oxidation, the smaller is the region in which the particles are formed and therefore also the regions in which the aerosol-induced radiation effects are found. Furthermore, the probability that radiation-absorbing trace substances (e.g. soot) are incorporated is increased and the reflectivity of the aerosol is reduced. Thus, this process as well adds to NO_x and positive radiative forcing in the atmosphere. Quantifying this effect is not possible since this process involves a series of non-linear steps which are coupled to one another (e.g. the influence of the concentration of OH radicals on the particle nucleation rate) and which are of course spatially very heterogeneous (e.g. due to cloud patterns).

3 Attempt at Performing a Quantification and Summary

The effects discussed are summarized and presented schematically in **Fig. 1**.

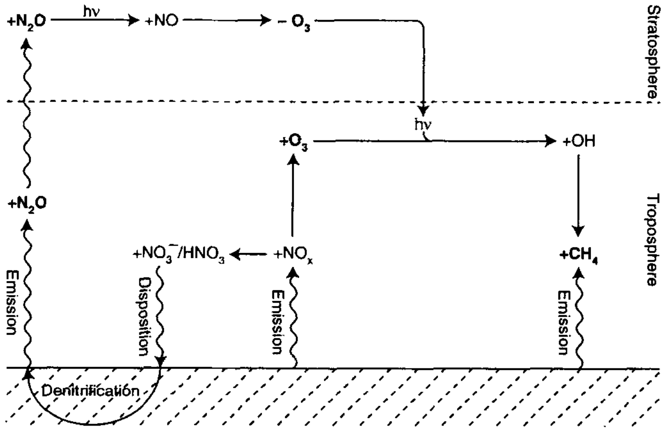

Fig. 1: Schematic display of the important effects of atmospheric chemistry and others in connection with the greenhouse effect of NO_x. Atmospheric trace gas concentrations are represented by a preceding sign which represents their predominant trend and by their chemical formula. (The trend for the OH radical is not uniform throughout the troposphere; see text.) Greenhouse gases are printed in bold-faced type. hv = photochemically effective radiation. Connecting lines indicate strengthening (arrows) or weakening (dots) interactions.

A compilation of the discussed effects shows that the indirect greenhouse effect of NO_x emissions causes positive radiative forcing, i.e. it causes a rise in the temperature of the atmosphere (→ *Table 3*).

It is dominated by NO_x role as a catalyst in the tropospheric production of ozone. The additional emission of N_2O from soils, which is caused by the deposition of nitric acid and nitrate, is less important. In this case, however, a short-term burden (life span of NO_x and subsequent products in the atmosphere: several days) is converted into a long-term burden (the residence time of N_2O is 120 years; N_2O is photolyzed in the stratosphere and enhances the depletion of the ozone layer there).

Table 3: Indirect greenhouse effect of global NO_x emissions via various reaction pathways

Influence of NO_x (as NO_2) on	sign	GWP[a] Greenhouse warming potential (temporal horizon of 20/100 years)
production of tropospheric O_3	+	30[b]/ 7[b]
degradation of stratospheric O_3	–	<0.05/< 0.24
influence on tropospheric CH_4	(+)	negligible
production of tropospheric N_2O	+	0.38 – 3.8/0.41 – 4.1
acceleration of aerosol formation	+	unknown

[a] A unit for measurement of the greenhouse effect relative to the emission of the same mass of CO_2

[b] The greenhouse effect of NO_x emissions due to air traffic is approximately a factor of 30 times higher

The greenhouse potential of NO_x with an estimated GWP (NO_x) = 30 – 33 for a time horizon of 20 years and with an estimated GWP (NOx) = 7 – 10 for a time horizon of 100 years is thereby comparable in magnitude with that of methane (IPCC 1990; BRÜHL 1993). Man produces (275 ± 75) × 10^{12} g CH_4/year (IPCC, 1992) and, at present, about (100 + 29) × 10^{12} g NOx/year (as NO_2). In case that NOx is emitted from air traffic, a substantially higher greenhouse effect is expected (approximately a factor of 30 higher). For these specifications, an uncertainty of approximately 50 % must be assumed.

Table 4: Values of the individual sectors in Germany 1990 (BMU 1993; values in 10^{12} g CO_2 equivalents)

GWP[(a)]	Sum	CO_2 1	CH_4 63	N_2O 290	NO_X 126 (60 – 268)
Fossil fuels	1270	1008	96	6.3	160 (76 – 340)
of this from traffic	310	194		2.6	113 (54 – 241)
Production processes	30			30	
Agriculture	≈ 180	≈ 30	129	21	< 13
Waste management	140		140		
Others	47	23	16	8.2	
All sectors	1670	1061	381	68	160 (76 – 353)

(a) Temporal horizon of 20 years. The NO_X values are based upon the estimates cited in Section 2.1

An estimate of the greenhouse effect caused in Germany (in CO_2 equivalents; *Table 4*) shows that the consideration of the indirect greenhouse effect of NO_x increases the sum of all anthropogenic portions by 10 (5 – 21) % to approximately 1670 CO_2 equivalents and that the portion of the traffic sector increased from 13 to 19 (16 – 24)%.

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