Nitrogen Oxide Emissions from Air Traffic

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Abstract. About 153 million metric tons of aviation fuel were consumed in 1987, which was *ca.* 13% of the world's consumption of transportation fuel. Burning this fuel produced *ca.* 2.75 million tons of nitrogen oxides, calculated as NO_2, using an average emission index EI of 18 g NO_2 per kg fuel. 0.92 million tons of NO_2 was exhausted between 9 and 13 km, which is an especially endangered altitude range, estimated with an EI of 15 g NO_2 per kg fuel. Air traffic is the main NO_x source between 9 and 13 km. Since the NO_x background concentration at this altitude is low and the possible lifetime of an admixture two orders of magnitude larger compared to the ground, these NO_x emissions can lead to an important increase of tropospheric ozone, which contributes to the global greenhouse warming. Alternatively, NO_x emitted in the lower stratosphere may contribute to stratospheric ozone depletion, especially at high latitudes.

1. Nitrogen Oxides at Different Altitudes

Nitrogen oxides emitted near the ground are removed from the atmosphere within days mainly as nitric acid. This is also true for most of the 2–10 million tons N (6.5–33 million tons NO_2) per year from lightning estimated by *Crutzen* and *Müller* [1]. Opposed to that, NO_x admixtures near 10 km altitude, according to *Fabian* [2] [3], have a lifetime which is about 100 times longer and, therefore, contribute more to the chemistry of the atmosphere. At 15 km, the concentration of NO_x is about one order of magnitude lower than at 25 km. Results of NO_x measurements between 9 and 13 km at different latitudes are not available.

The naturally produced stratospheric nitrogen oxides, 0.5–1.5 million tons N (1.6–5 million tons NO_2) per year according to *Crutzen* and *Müller* [1] are mainly formed from N_2O above 20 km. Catalytic reaction cycles involving these nitric oxides are the main sink for stratospheric ozone in the unperturbed atmosphere.

2. Possible Consequences of Air Traffic Emissions at High Altitudes

The anthropogenic nitrogen oxide emissions above 9 km are of special concern regarding the global climate. Between 9 and 13 km, they are almost entirely from

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air traffic [4]. Catalytic converters for NO_x are not employed in jet engines because of high working temperatures occurring there and the high exhaust velocities. It should be emphasized that according to *Grassl* [5] ozone depletion above the northern hemisphere is about twice as high as calculated with chlorofluorocarbon (CFC) climate models, which do not include nitrogen-oxide emissions from aviation. *Staehelin* and *Dütsch* [6] also come to the conclusion that only half of the stratospheric ozone depletion can be explained by perturbations of photochemistry caused by CFCs. (They attribute the remaining half to changes in circulation.) Their measurements above Arosa showed a 3% ozone depletion 1966–1987 between 10.5 and 22 km altitude (5% over all altitudes above 10.5 km), that is in the region disturbed by air traffic. (A planned supersonic air fleet of 600–1200 planes at altitudes of 16–35 km would cause an additional threat to the ozone layer.) Depending on latitude and season, the minimum heights for ozone depletion by NO_x are between 10 and 18 km with lowest altitudes in winter at high latitudes [7] [8]. Below this variable altitude limit and in the troposphere, nitrogen oxides catalyse the photochemical ozone production.

It should also be mentioned that, above *ca.* 9 km altitude, water vapour from exhaust gases may influence the climate, especially by forming condensation trails of cirrus ice crystals. Cirrus clouds contribute to the global greenhouse warming [7]. 1.25 kg of water vapour are produced from 1 kg of fuel. This gives for 1987 a contribution of 77 million metric tons of additional water vapour above 9 km by air traffic (see *Chapt. 5*).

3. Interactions of Nitrogen Oxides and Ozone

Anthropogenic nitrogen oxide emissions are responsible for increased tropospheric ozone [3] [6] [8] [9]. Ozone at that altitude, because of its infrared absorption, contributes to the global greenhouse warming [10].

In the stratosphere, on the other hand, ozone is produced from oxygen by absorption of energetic UV radiation. At the same time stratospheric ozone is catalytically destroyed by NO_x radicals. This results in a stationary state ozone concentration [1] [2] [6] [10] [11]. Additional anthropogenic NO_x and especially CFCs will decrease the stationary state value. Stratospheric water vapour (*via* hydroxyl radicals) and other trace gases also contribute to ozone destruction [1]. Stratospheric photochemistry is comprehensively described by *Crutzen* and *Müller* [1] as well as by *Staehelin* and *Dütsch* [6].

4. Nitrogen Oxides and the Ozone-Hole Theory

According to the present state of knowledge [1] [3] [8] [11–13], a key reaction above *ca.* 25 km is the photolytic formation of halogen radicals from CFCs and other halogenated hydrocarbons under the influence of short wave solar UV radiation. The most important halogen radicals are

atomic chlorine and chlorine oxide. These can catalytically destroy ozone, although they mainly react with CH_4 and NO_2 to form HCl and $ClONO_2$, respectively:

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (1)$$
$$ClO + NO_2 \rightarrow ClONO_2 \qquad (2)$$
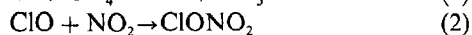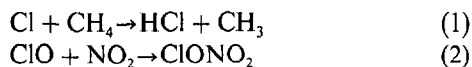
These substances slowly reach lower altitudes.

Crutzen and *Arnold* [11–13] identified the formation of polar stratospheric clouds as the main cause for the antarctic ozone hole. These result from the freezing-out of nitric acid trihydrate crystals between 12 and 22 km altitude at temperatures below $-80°$. On the particle surface three chlorine species: Cl_2, HClO, and ClONO are formed from the reaction of HCl and $ClONO_2$:

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3 \qquad (3)$$
$$HCl + ClONO_2 \rightarrow HClO + ClONO \qquad (4)$$
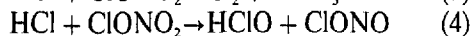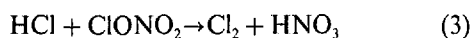
These molecules dissociate to form chlorine radicals at the end of the polar winter under the influence of sunlight. They catalytically destroy ozone *via* ClO radicals with a rate depending on the square of the ClO concentration leading to the so-called ozone hole and a temperature decrease in the stratosphere. It is not clear, however, how much anthropogenic NO_x emissions above 9 km contribute to the formation of polar stratospheric clouds and, therefore, to the ozone hole.

5. Fuel Consumption of Air Traffic

The *Table* shows the global consumption of mineral oil products given by *IEA* [14] (predictions based on a *FAA* projection [15] in parenthesis). The data allow emission estimates, by using emission indices.

According to *Kavanaugh* [16], 40% of all fuel used for air transport is burnt above 9 km. Military consumption contributes *ca.* 24% to the total fuel consumption. One reason for the steep increase of aviation fuel consumption is probably the low price of US$ –.16 per liter of kerosene (average over the last tree years). This is a consequence of the international tax exemption.

6. Estimates of Nitrogen-Oxide Emission Indices

An investigation into literature (till end of 1989, *CA* till August 20, 1990) of the data banks *CA*, *ULIDAT*, and *NTIS* led to the following conclusion:

Assuming the scientifically based and calculated *EI* values published by *Lecht et al.* [17] and attributing 40% of the global fuel consumption to altitudes above 9000 m, 12% to 'landing and take-off cycle' (*LTO*) and 48% to all heights between 915 and 9000 m, a weighted average emission index of 18 ± 3 g NO_x per kg fuel, calcu-

Table. *Fuel Consumption* (in thousand metric tons)

Year	All products	Fuels	
		Transport (tot.)	Aviation
1971	2267822	760011	99462
1977	2852555	976064	117246
1985	2736676	1115875	141278
1987	2860100	1180613	153218
1990			(176500)

lated as NO_2 is resulting. For altitudes above 9000 m, an emission index of 15 ± 3 g NO_x per kg fuel is resulting. (At altitudes, no measured values are available.) The following papers deal with emission indices:

The *US Environmental Protection Agency* [18] calculated the emissions from *LTO* up to 915 m for different types of engines and planes based on the *ICAO Exhaust Emissions Data Bank* sheets. From that study, *EI* values for the *LTO* flight phase can be calculated. For the most important civil engines, the average is *ca.* 15 g NO_x per kg fuel. The decisive data for flight altitudes above 915 m and for cruises are missing like in the *ICAO* sheets. (A more recent edition of this compilation was not available till March 1990.)

Lecht et al. [17] calculated the height dependence of the emissions from the 11 engines mostly used in the FRG in 1984 based on the *ICAO Exhaust Emissions Data Bank* sheets. The calculations rely on several assumptions, so that experimental checks still need to be done. The average *EI* for 100% thrust is 27.8 g NO_x per kg for the 11 types of engines considered (4 of the 11 are *PW-JT8D* types). For the 5 large engines above 110 kN power, *EI* is 38.7 g and for the 6 engines below 110 kN 18.8 g NO_x per kg. According to this study, the nitrogen oxide emissions per kg of fuel increase with increasing flight height at a given thrust. Since the thrust strongly decreases with increasing height, however, lower total NO_x emissions per kg of fuel are resulting. From the tables of this study for flight altitudes between 915 and 9144 m, a weighted *EI* of about 21 g NO_x per kg is estimated at an estimated average thrust of about 40%, an *EI* value of about 15 g NO_x per kg at a thrust of 25% at higher altitudes.

Weyrauther et al. [19] give the fuel consumption and nitrogen-oxide emission of air traffic above the FRG. However, the data do not allow a reliable estimate of the emission index values.

Oliver et al. [20] gave in 1977 for a cruise altitude of 9–12 km for old, low-compression engines an *EI* of 6 g NO_x per kg and for more modern engines 16 g NO_x per kg fuel.

Kavanaugh [16], in cooperation with the air traffic industry and the *US Environmental Protection Agency*, calculated with a global aviation fuel consumption of 98 million tons for 1980 instead of the correct value of *ca.* 130 million tons and with 100 million tons for 1990 instead of the probable 176 million tons. He uses for all flight conditions the same *EI* of 10.9 g NO_x per kg, calculated for cruise conditions, apply-

ing a questionable empirical formula given by *Bohick* [21]. *Kavanaugh* assumes a decrease of the *EI* of 11% till 2025 due to improved engines. Furthermore, he mentions that the mostly used engines *PW-JT8D* consumed in 1980 *ca.* 33% of the global aviation fuel.

Kinnison and *Wuebbles* [22] give an *EI* of 14 g NO_x per kg at altitudes between 12 and 34 km for a US supersonic project.

Bula [23] from the *Swiss Federal Civil Aviation Office* assumes for 1988 en *EI* of 15.2 g per kg for *LTO* and an *EI* of 19.6 g per kg as weighted average for the total amount of fuel burnt above Switzerland.

Johnston et al. [24] used an *EI* of 40 g NO_x per kg fuel for current high-performance commercial aircraft, flying at about 12 km altitude (taken from a *NASA* report).

7. Nitrogen-Oxide Emission Estimates above 9 km and in Total

Calculated as NO_2 with an average weighted emission index *EI* of 18 g NO_x per kg fuel the total global NO_x production from air traffic in 1987 is *ca.* 2.75 million metric tons (1990 probably about 3.2 million tons). With the *EI* valid above 9 km of *ca.* 15 g NO_x per kg, the nitrogen-oxide emission between 9 and 13 km is *ca.* 0.92 million tons (1990 probably 1 million tons). This is of a similar magnitude as the yearly natural NO_y flux ($NO_x + HNO_3$) coming down from the stratosphere, which is *ca.* 0.3–0.9 million tons N (1–3 million tons NO_2), according to *Ehhalt* and *Drummond* [25].

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Rückblick auf 40 Jahre Chemieunterricht

(nach einem vor der Berner Chemischen Gesellschaft gehaltenen Vortrag)

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Im Herbst 1948 habe ich meine Tätigkeit als Chemielehrer begonnen. Ich möchte Ihnen einiges über meine Erfahrungen oder Erlebnisse aus den vergangenen vierzig Jahren berichten. Es soll kein 'wissenschaftlicher' Beitrag sein, sondern eine 'Plauderei'. Bedenken Sie bitte, dass ich von meinen *persönlichen* Erfahrungen berichte, von meiner Schule, von meinen Schülern und von meinem persönlichen Standpunkt aus. Andere Kollegen würden vielleicht ganz andere Dinge berichten oder andere Schwerpunkte setzen.

Also, im Herbst 1948 habe ich angefangen. Ich war damals Doktorand an der ETH. In Winterthur, an der Schule, wo ich selbst zur Schule gegangen bin (und ich mir nach der Maturität vorgenommen hatte, nie mehr einen Fuss in das Schulhaus zu setzen; so hatte ich genug von der Schule!) suchte man einen *Hilfslehrer*, um eine Klasse in Chemie zu unterrichten. Ein Kollege aus unserem ETH-Institut, der bereits in Winterthur als Hilfslehrer tätig war, fragte mich an, ob ich die Klasse übernehmen wolle. 'Man kann ja den Versuch wagen', war meine Meinung, obschon ich eigentlich nicht die Absicht gehabt hatte, das

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Lehramt als Beruf zu wählen und dementsprechend auch keine Minute didaktischer Ausbildung genossen hatte. (Böse Zungen werden vielleicht sagen: 'Aha, das merkt man heute noch!'). Ich sagte zu und begann nach den Herbstferien – nach 3 Wochen WK – meinen Unterricht. Mit sehr grosser Angst, muss ich gestehen, denn meine Schwester charakterisierte meine zukünftige Klasse als eine der schlimmsten in der Schule. Ich war meiner Sache gar nicht sicher und war fast überzeugt zu scheitern; niemandem durfte deshalb von meiner zukünftigen Lehrtätigkeit erzählt werden. Ich erinnere mich noch sehr gut an meine erste Stunde und an die Gefühle, mit denen ich zum Schulhaus ging: die Stunde kam mir lang vor; ich hatte zuwenig vorbereitet und der Stoff ging mir fünf Minuten vor Schluss aus. Die Klasse war aber überaus brav.

Im folgenden Frühjahr musste ich noch drei weitere Klassen übernehmen; ich fühlte mich allmählich sicherer, und das Unterrichten begann mir Freude zu machen. Die Situation war damals ganz ähnlich wie heute: *Der* Chemielehrer der Schule stand kurz vor der Pensionierung; vielleicht schätzten die Schüler den frischeren, vielleicht auch konsequenteren Unterricht des jungen Doktoranden.

Bevor ich dazu übergehe, von meinen Erfahrungen und Erlebnissen zu berichten,

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1974 Berufung an den neugeschaffenen Lehrstuhl für Didaktik der Chemie an der Universität Tübingen. 1975 Lehrauftrag in Tübingen. Ablehnung des Rufes.

Verfasser zahlreicher Lehrbücher für Schule und Hochschule, zuletzt 'Chemieunterricht - eine praxisorientierte Didaktik' (1990). Die letzte Bearbeitung der 'Grundlagen der organischen Chemie' erfolgte gemeinsam mit F. Vögtle in Bonn ('Organische Chemie – Von den Grundlagen zur Forschung', 2 Bände). Mitherausgeber der Zeitschrift 'Chemie in Labor und Biotechnologie'. Verschiedene Veröffentlichungen über Limnologie und farblose Flagellaten. Träger der Gmelin-Beilstein-Denkmünze der GDCh für Verdienste um die chemische Literatur (1976) und Ehrenmitglied des Institut Grand Ducal de Luxembourg, Section Sciences (1982).

möchte ich kurz einige allgemeine Gesichtspunkte beleuchten. Bitte bedenken Sie nochmals, dass ich auch hier von meinen persönlichen Erfahrungen berichten muss; meine Feststellungen haben also keineswegs Allgemeingültigkeit. Winterthur ist eben keine Großstadt, und wir haben viele Schüler, die aus der umliegenden Landschaft kommen. Zudem ist unsere Schule – ein 4^1/$_2$-jähriges Gymnasium – in mancher Hinsicht eine 'Aufstiegsschule'.