Anthropogenic sources of air pollutants.

Part 1: Fundamentals

(4th lecture)

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Objectives:

To describe the different man-made processes and sources of trace substances into the atmosphere and which substances in which amount are entering the air and change it composition.

- definitions
- causes of air pollution
- energy conversion (power plants)
- agricultural activities
- traffic (fuel burning)
- others

Emission (from latin: emittere - *escaping*) means

a) the process of releasing substances (and radiation) from a given source,

b) the flux of matter Q in terms of [mass·time^{-1}].

A specific emission is defined related to the source and also called emission factor f.

Sources are separated into

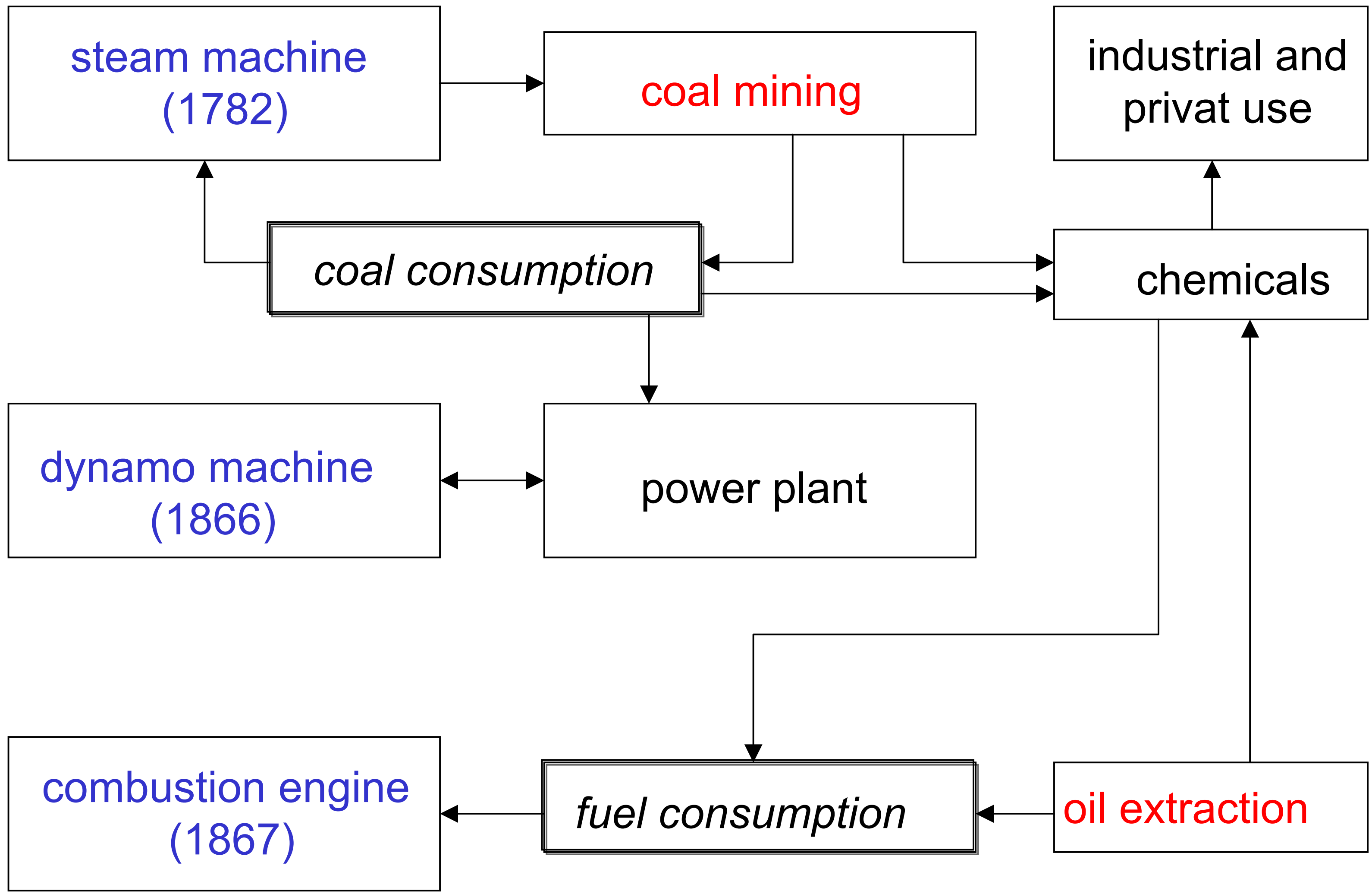
- point sources (e.g. power plant stack),
- square (diffuse) sources (e.g. rice paddy),
- surface and altitude sources,
- mobile and stationary sources.

Cause of emissions:

a) Chemical and biochemical conversion processes (including combustion) in open systems with gradients in concentration, pressure, temperature,
b) matter transport in open systems by wind (dust whirl-up),
c) evaporation (of volatile substances).

☞ *To avoid emissions, one has to taken care on*

- high conversion rates of processes,
- alternative (substituting) technologies/substances,
- physical instead of chemical processing,
- closed processing systems (containment),
- clean areas (no open disposal sites),
- solvent-free product use.

Pollutants	The era of fossil fuel use
dust/PM SO_2 HCl CO_2 soot CO, VOC Soot PM	

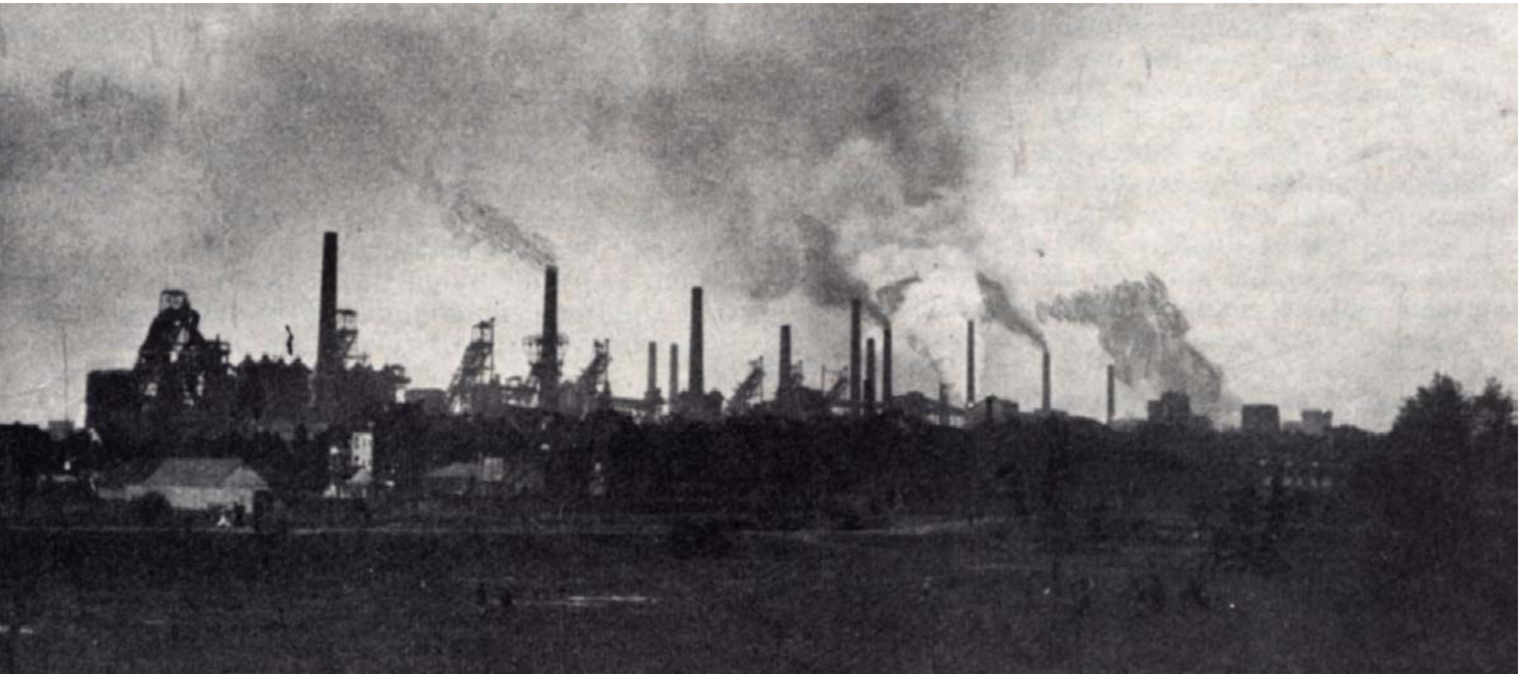
Industrial landscape in Germany, about 1860 (painting)

The importance of smoking stacks...

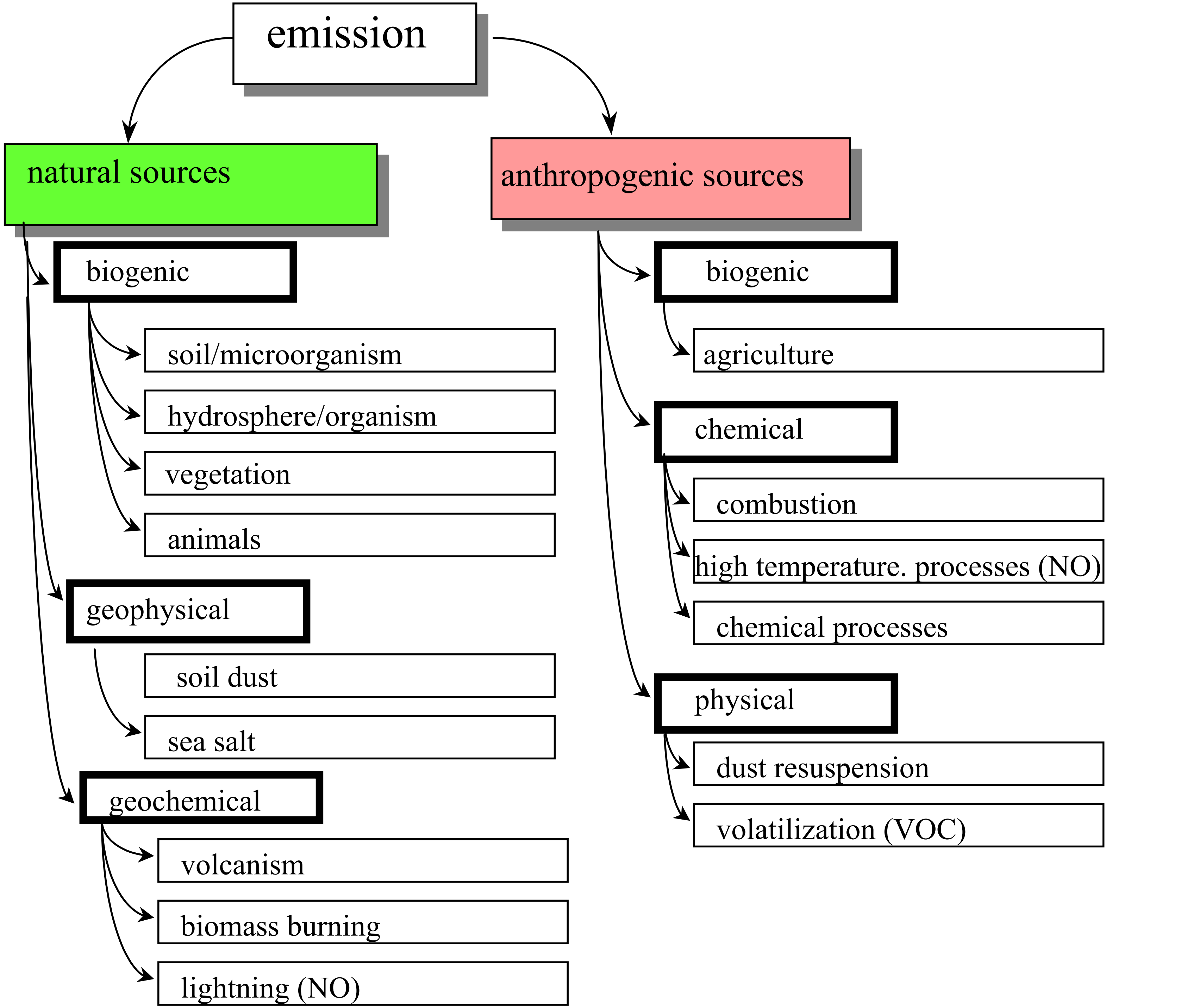
A political satirical painting from the journal „Simplicissimus“ showing the power of workers to „capitalists“.

Smoking stacks means profite but also work to peoble...

Ostrava in Czech Republic, about 1963



Industrial skyline of Duisburg (Ruhr area, Germany), about 1955


emission
natural sources
biogenic
soil/microorganism
hydrosphere/organism
vegetation
animals
geophysical
soil dust
sea salt
geochemical
volcanism
biomass burning
lightning (NO)
anthropogenic sources
biogenic
agriculture
chemical
combustion
high temperature. processes (NO)
chemical processes
physical
dust resuspension
volatilization (VOC)

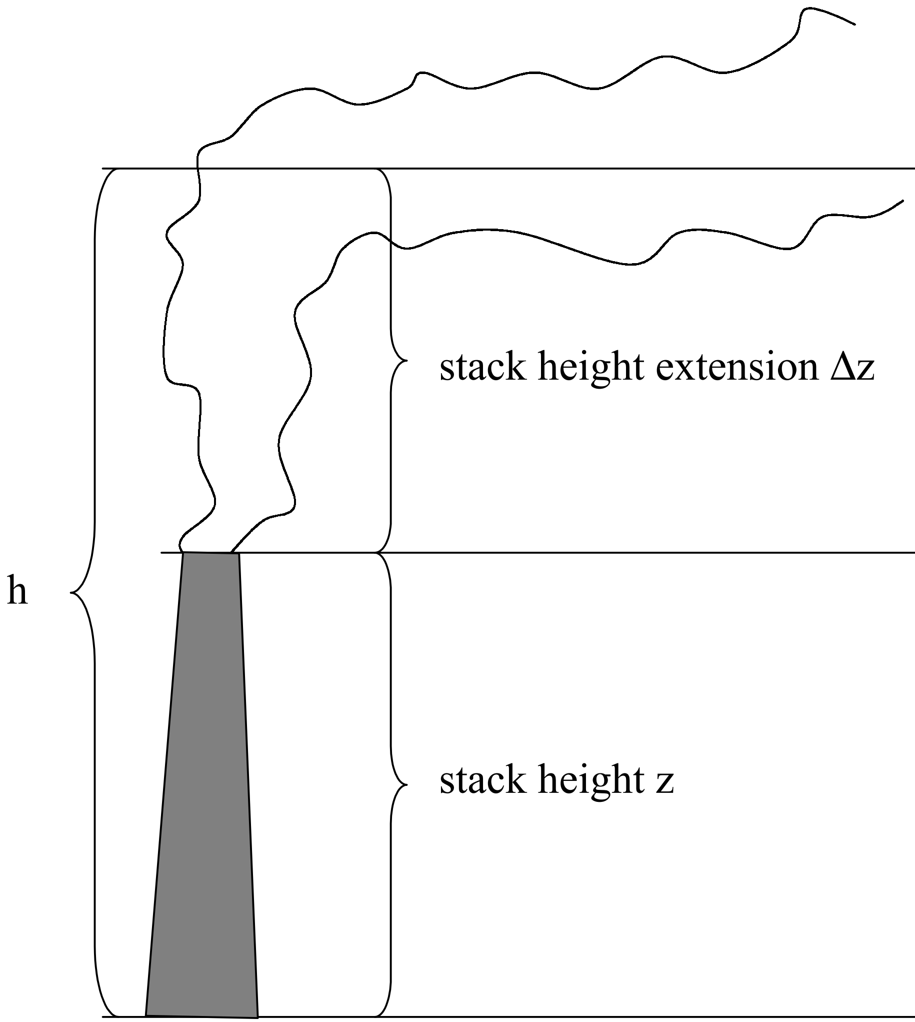
Three causes of increasing atmospheric pollutants:

Agriculture (food production)
on the basis of **fertilizer application**

Energy „production“
on the basis of **fossil fuels**

Growth of the world population and
increase of per-capita **consumption** of resources

emission altitude $h = z + \Delta z$



$$Q = f \cdot M$$

$$f = \left(1 - \frac{\alpha}{100}\right) \cdot \left(1 - \frac{\gamma}{100}\right) \cdot \frac{S}{100}$$

Q emission (flux)
f emission factor
S sulphur content (in %)
α sulphur bonding in ash
γ degree of desulphurization
M mass of burned coal per time

Emission factors for SO_2 (in kg SO_2 t^{-1} fuel and product, resp.)

fuel and product, resp.	Möller (1985)	Wolf and Hidy (1997)	
		no control	with control
hard coal	35.6 (±5.8)	36-44[a]	7-9[a]
brown coal	16.8 (±5.2)	-	-
crude oil destillate	-	2.07	-
heating oil	21.3 (±5.7)	30	6.3
concrete production	-	0.89	0.71
Cu mining (smelting)	2000	2405	398
Zn mining (smelting)	100	912	21
paper production	-	2	1

[a] recalculated from t oil equivalent into t hard coal equivalent

Matter budget of lignite power plants Lübbenau (1300 MW, mean 1971-1980) and Thierbach (800 MW, mean 1975-1980) in kt a^{-1}; after Möller et al. (1985); Lübbenau has been closed in 1992

flux	KW Lübbenau[a]	KW Thierbach[b]
burned coal	12547(±374)	5437(±81)
ash content	1395(±48)	561(±86)
coal sulphur	157(±40)	101(±6,5)
burner ash	1395(±180)	203(±103)
filterash 1st stage	50(±8)	10(±1,6)
filterash 2nd stage	853(±136)	277(±45)
filterash 3rd stage	100(±16)	45(±7,3)
filterash 4st stage	50(±8)	14(±2,3)
flue gas dust (emission)	79(±31)	13(±2,8)
SO_2 emission (as S)	138(±40)	78(±4)
S bonding (burner ash)	3.4(±2,3)	19.5(±7,6)
S bonding (filterash)	13.6(±8,1)	3.0(±0,5)
S bonding (flue gas dust)	2.0(±1,0)	0.28(±0,05)

[a] ash content 11.1 %, sulphur content 1.1%
[b] ash content 10.3 %, sulphur content 1.9%

.

88% and 77%, resp. of coal sulfur has been emitted!

Mean percentage of flue gas desulphurization for coal-fired power plants based on total installed capacity (in %), after Lehfohn et al. (1999)

Country	1973	1980	1985	1990	1997
Japan	90,0	88,6	89,6	89,9	?
USA	80,3	82,4	84,9	85,0	?
Germany[c]		85,0[a]	89,8	90,6	100
Sweden			72,9	75,8	?
Austria		55[b]	85,2	90,7	?
Canada			30,0	74,1	?
Finnland				91,2	?
France				83,5	?

[a] 1981
[b] 1982
[c] before 1990 only Westgermany

Nowaday we can assume 100% installed desulphurization capacity in the „industrialized world“

Global and European emissions in percentages (%) of total emission and total emission (in Tg yr^{-1}), based on 1995; after Lenz and Cozzarini (1999)

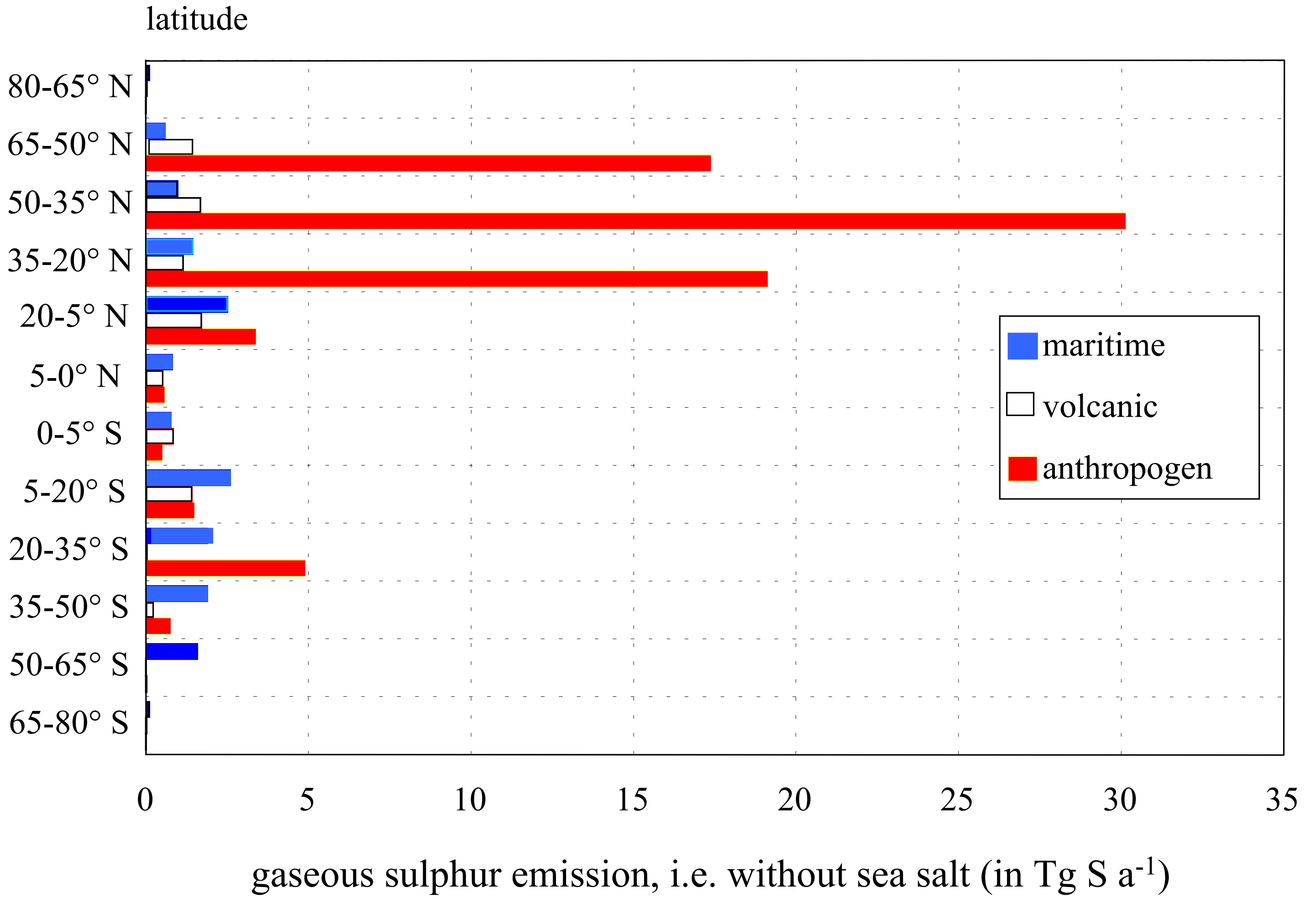
Source	global				Europe				
	CO_2	CH_4	N_2O	NO	NMVOC	SO_2	CO	NO	PM_{10}
Industry	22	20[b]	10	14	19	24	12	10	25
Power plants	30	-	-	29	-	61	-	15	16
Agriculture	-	64	47	8	6	-	-	22	13
Municipial	27[a]	14[c]	9[d]	8	29[g]	8[a]	17[a, h]	3	11[a]
Traffics	21	< 1	5	33	44	6	68	50	30
Others	-	1	29[e]	6[f]	2	1	3	-	5
Total	25000	346	15	72	13.5	12	45	10.4	2.4

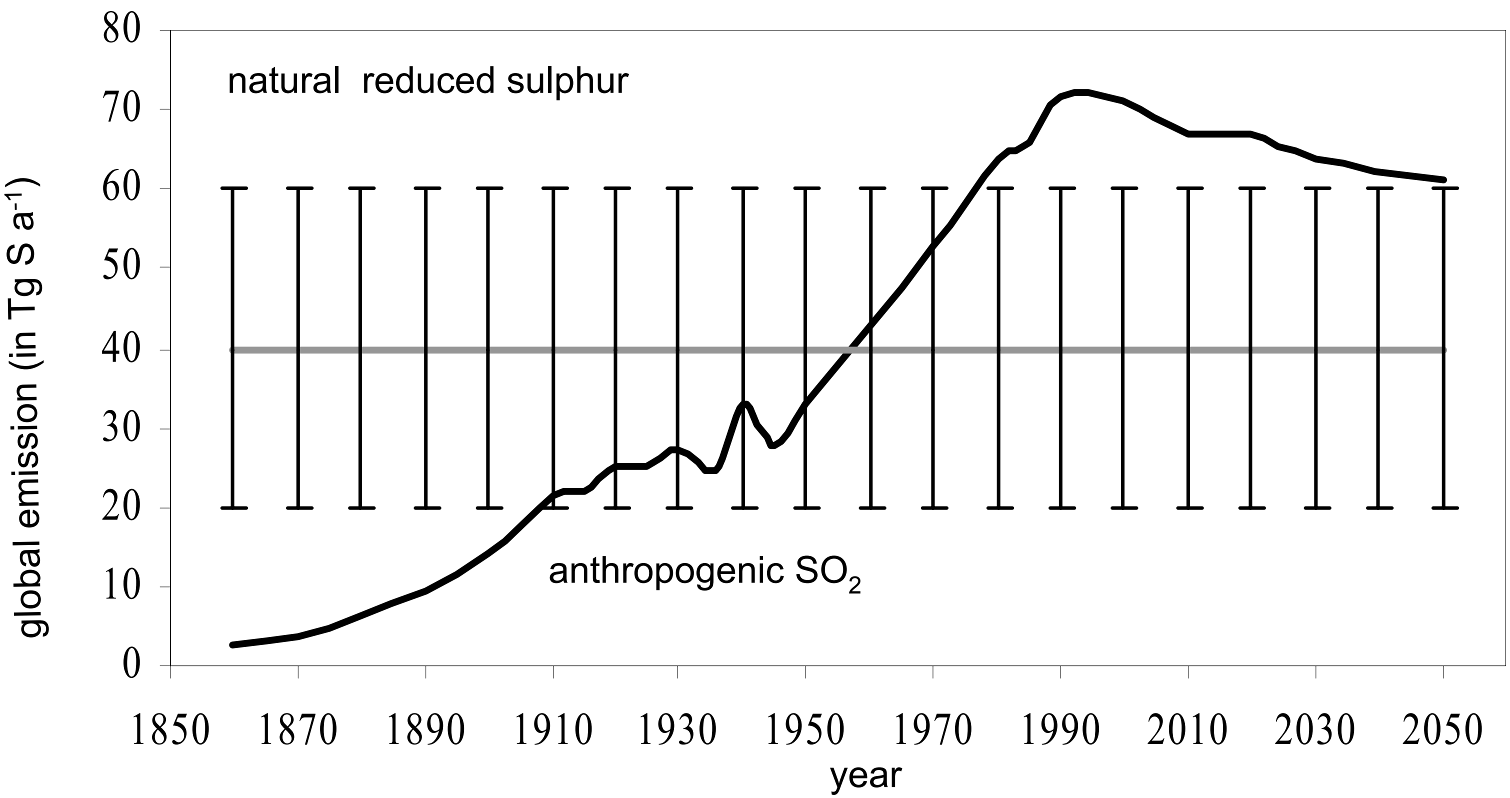
[a] house burning
[b] production and use of fossil fuels
[c] landfills
[d] ground water
[e] deforestization in tropics
[f] atmospheric NH_3 oxidation
[g] solvent use
[h] disposal incineration (5%)

Global natural and anthropogenic emissions (in Tg a^{-1} element, with exception of PM), after Möller (2003)

Substance	natural	anthropogen (around 1990)[a]
CO_2	120000[b]	7000
CO	650 (± 150)	400
CH_4	150 (± 30)	226
NMVOC	55 (± 25)	153
Terpene	600 (± 300)	-
NH_3	25 (± 5)	30
N_2O	15 (± 3)	4-8
NO	20 (± 2)	50
SO_2	13 (± 5)	70
red. S[c]	30 (± 6)	< 5
PM	3000 (± 1000)[d]	260-620[e]
Al[f]	40	7.2
Pb[f]	0.06	2.0

[a] large errors to be taken into account: 20% for SO_2, 100% for NMVOC)
[b] identical with uptake, i.e. photosysnthesis ≈ respiration
[c] DMS, H_2S, CS_2, COS et al.
[d] incl. sea salt and secundary particle formation
[e] incl. secundary particle formation (primary: 150-370)
[f] constituent of PM


latitude
80-65° N
65-50° N
50-35° N
35-20° N
20-5° N
5-0° N
0-5° S
5-20° S
20-35° S
35-50° S
50-65° S
65-80° S
maritime
volcanic
anthropogen
0
5
10
15
20
25
30
35
gaseous sulphur emission, i.e. without sea salt (in Tg S a-1)



natural reduced sulphur
anthropogenic SO_2
global emission (in Tg S a^{-1})
0
10
20
30
40
50
60
70
80
1850
1870
1890
1910
1930
1950
1970
1990
2010
2030
2050
year

Sulphur emission and comparison with resources

SO_2 emission in Tg S yr^{-1}

before 1970	1700
1971 - 2000	1900
2001 - 2030	1900
2031 - 2200	1000
after 2200	500 (?)
sum	7000

total sulphur in fossil fuels: 13.000 Tg (Meyer, 1970)

world sulphur resources (native & ores): 1400 Tg

global sulphur production in 2000 (Tg): 57 (about constant since 20 years)

global percentage of sulphur recovery from fossil fuels (mainly gas and oil), in %:

1950	0
1960	15
1970	32
1975	35
2000	50

global released sulphur until 2000 (Tg):

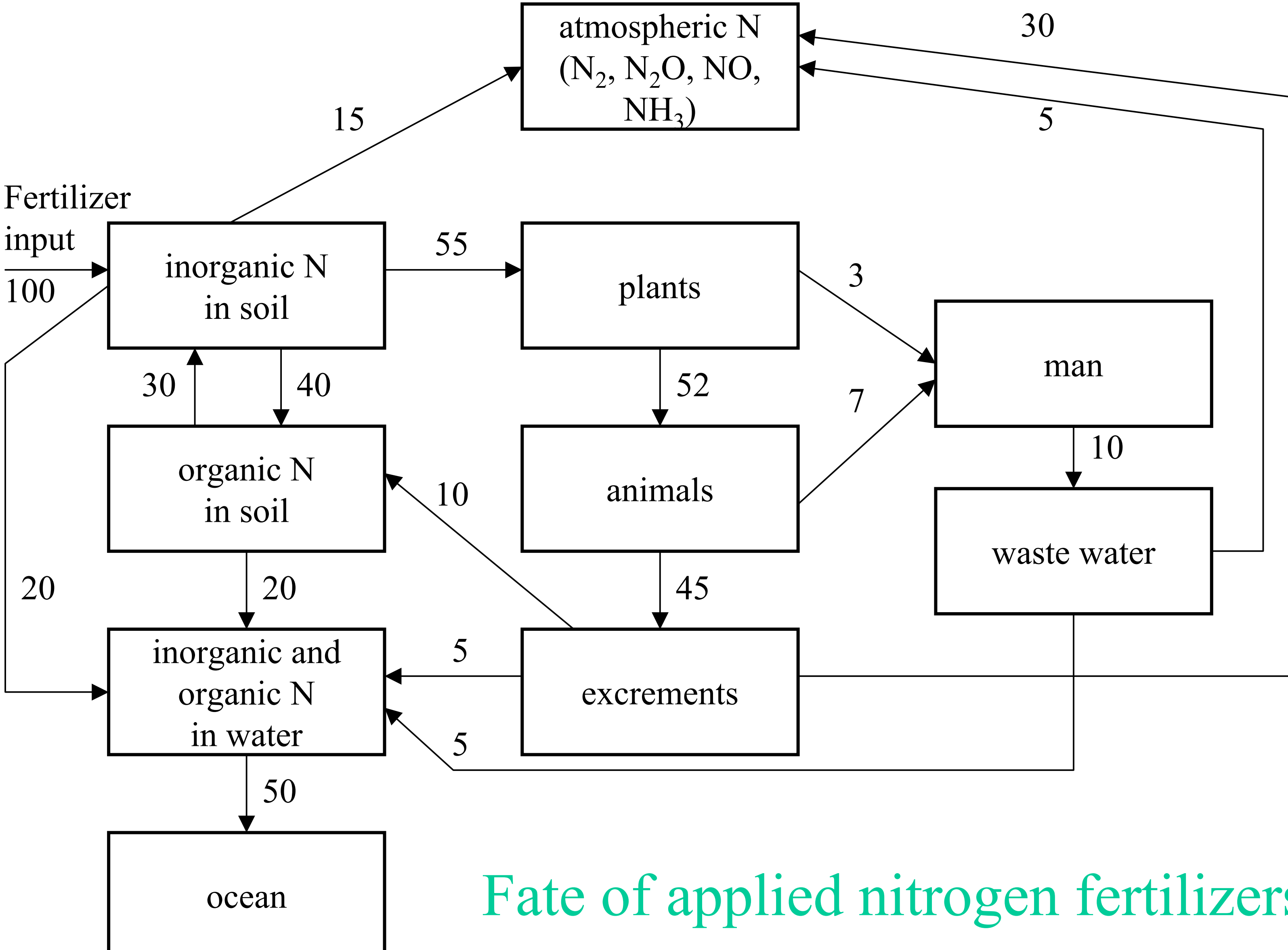
emission	3600
produced from primary resources	2600
produced from fossil fuels	800
recovered as gypsum from flue gas desulphurization	650

50% of global available reduced S has used (converted into sulphate)

Agriculture

Sources of emission:

- fertilizer application to farmland (N_2O, NH_3),
- rice paddies (CH_4),
- animals on gras and in stockhouses (NH_3 and others),
- soil dust by wind erosion and cultivation
- plants (NMVOC, bioaerosols)
- waste burning



Fate of applied nitrogen fertilizers

Global natural emission of NH_3 (in Tg N a^{-1})

source	Schlesinger and Hartley (1992)	Dentener and Crutzen (1994)	Friedrich and Obermeier (2000)
ocean	13	-	10
natural soils	10	5.1	2.9
wildlife animals	-	2.5	0.1
biomass burning	5	-	7.2
total	28	-	20

[a] have to considered being „anthropogenic“

NH_3 emission factors for animals and human (in kg yr^{-1})

Quelle	sources	A	B	C	D	E	F	G
Kühe	cows	13,64	22,1[a]	12,5/35,5[b]	22,9	23,04	14,3/28,5[b]	5,6/22[b]
Schweine	pigs	3,87	5,2	5,1	4,0/9,2[c]	5,36	6,4	4,0/4,3[c]
Geflügel	poultry	0,23	0,22	0,18/0,32[c]	0,18	0,25	0,32	0,2/0,4[c]
Pferde	hjorses	-	15,0	12,5	-	12,20	-	-
Schafe	sheeps	0,46	3,0	2,1	3,4	1,70	1,34	0,6
Haustiere[d]	domestic	-	-	-	-	-	0,5	-
Hase	hare	-	-	-	-	-	0,37	-
Rentier	ren	-	-	-	-	-	4,7	-
Mensch	humans	-	1,3	0,3	0,25	-	1,3(±50%)	-

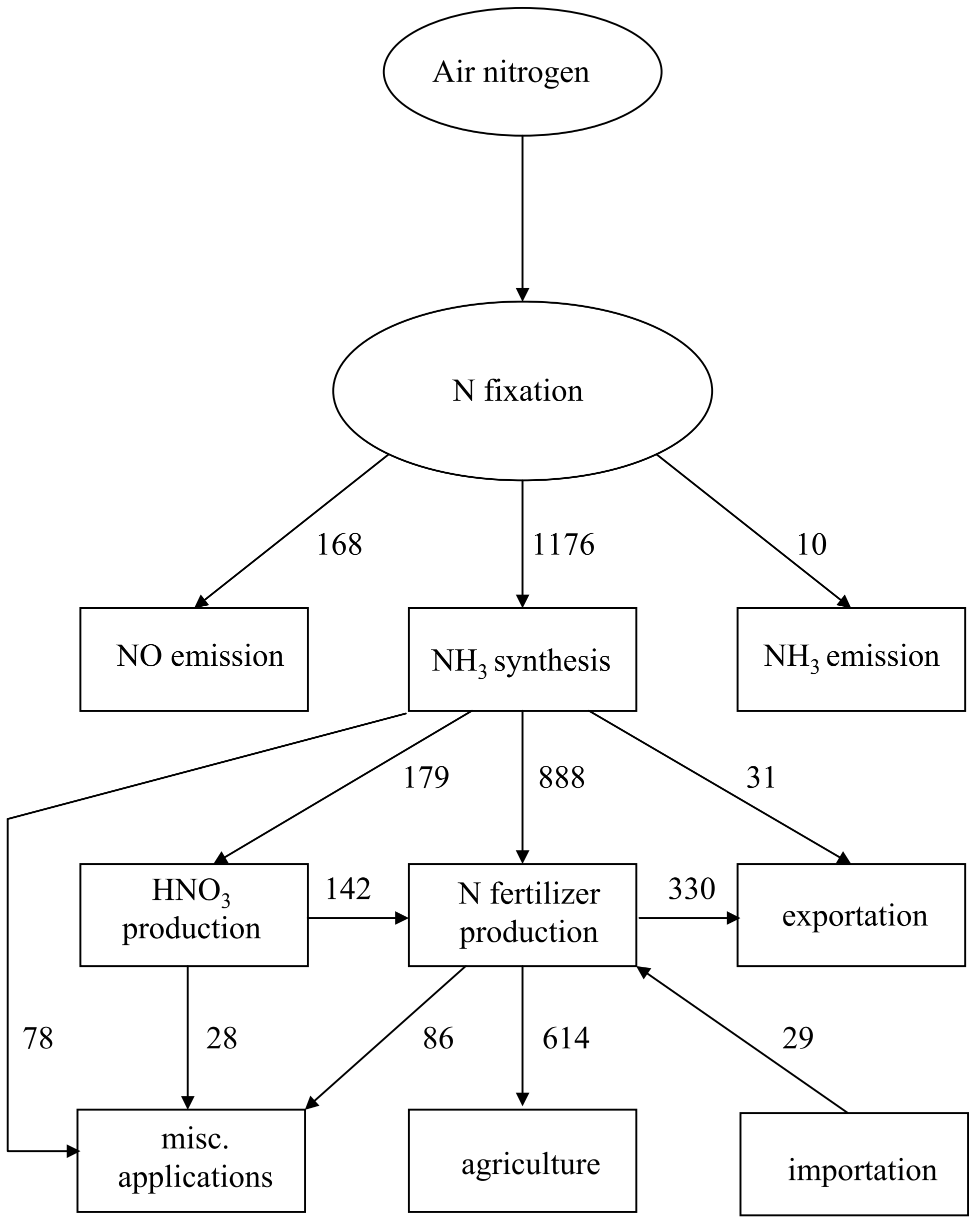
A: Buismann u.a. (1986), B: Möller und Schieferdecker(1989), C: Klaassen (1992),
D: Battye u.a. (1992), E: Kallweit (1995), F: Ryaboshapko (2001), G: Misselbrook u.a. (2001)

[a] Milchkühe 35,0, Mastkuh 15,4 (dairy/

[b] sonst. Kühe/Milchkuh (other cows/dairy)

[c] verschiedene Tierhaltung (Mastschwein/Sau, Hahn/Legehenne) – different animals (fattened pig/ sow, broiler/hen)

[d] Katzen und Hunde (cats/dogs)



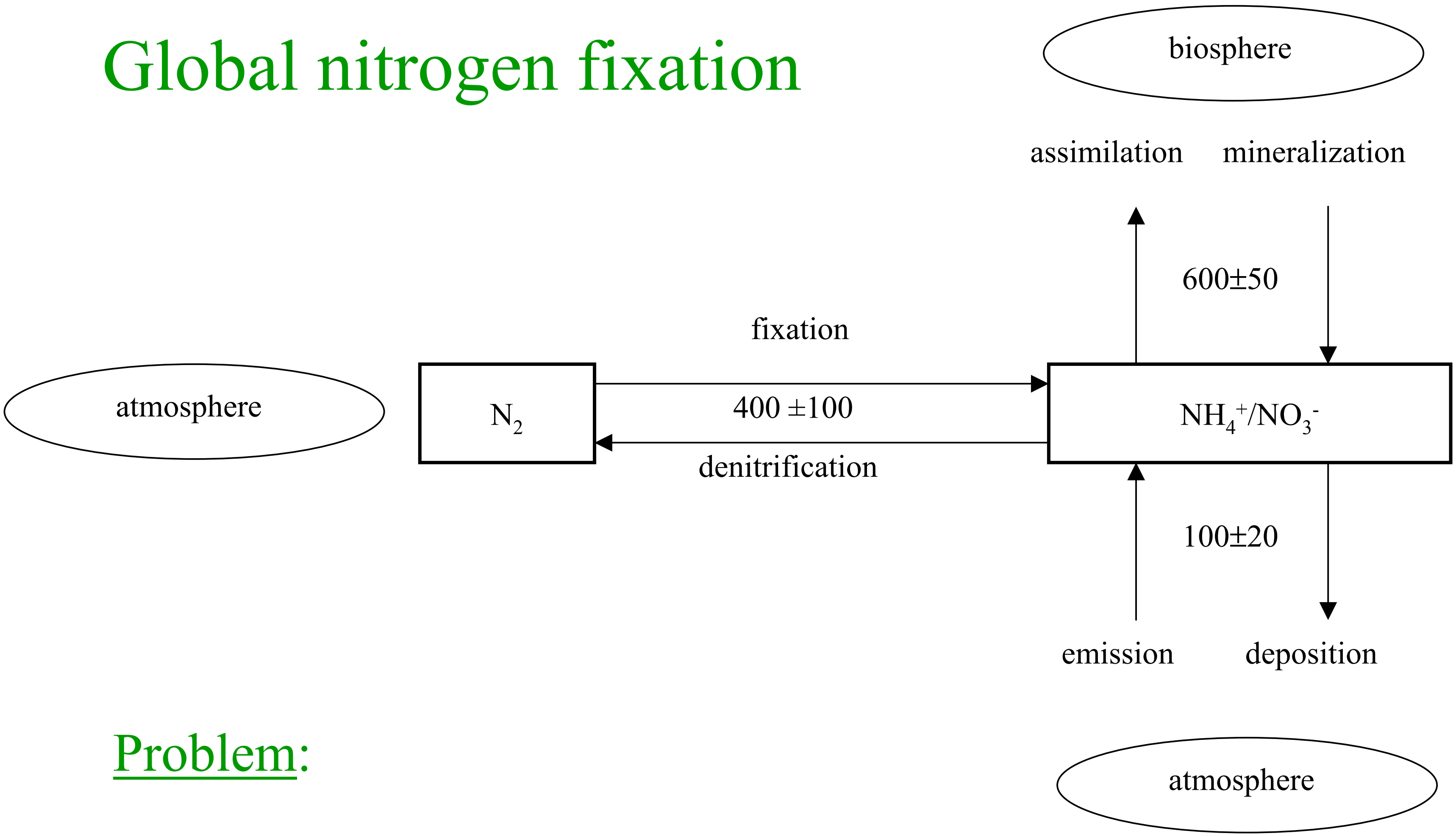
N flux through the industrial system of former Eastern Germany, 1980

(figures given as kt yr^{-1})

Global emissions of nitrogen compounds (in Tg N yr^{-1}), after Watts (2000)

source	NH_3	NO	N_2O
ocean (gases)	10-15	-	2
wet lands	-	-	-
natural soils and plants	3-5	4-8	8-10
wildlife	1-3	-	-
biomass burning	5-7	9	1
soil dust	-	-	-
seasalt	-	-	-
volcanism	-	-	-
lightning	-	4	-
secondary sources (NH_3 oxidation)	-	1-2	-
total (primary sources)	25(±5)	20(±2)	10(±3)
Global man-made sources	30(±10)	25(±5)	3(±1)

Global nitrogen fixation



<u>Problem</u>:

Amplifying by humans

Assessment of global biomass burning (in Tg a^{-1}), after Dignon (1995)

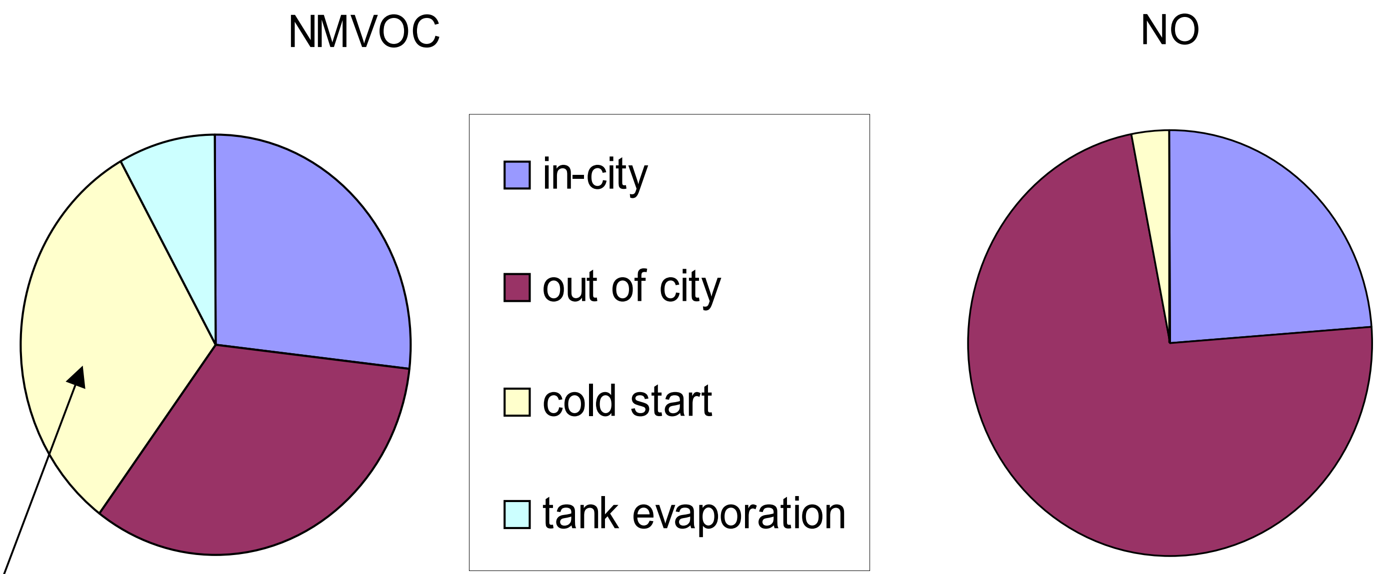
Component	Dignon (1995)	Malingreau and Zhuang (1998)
$C\text{-}CO_2$	1800-4740	3500
C-CO	350	350
$C\text{-}CH_4$	38	-
C-NMVOC	24	38
$N\text{-}N_2O$	0,8	0,8
N-NO	9	8,5
$N\text{-}NH_3$	5,3	5,3
$S\text{-}SO_2$	2,2	2,8
S-COS	0,09	0,09
$Cl\text{-}CH_3Cl$	-	0,51
H_2	-	19
OC (particulates)	60-80	69
BC (particulates)	7-10	19
PM, total	100-200	104

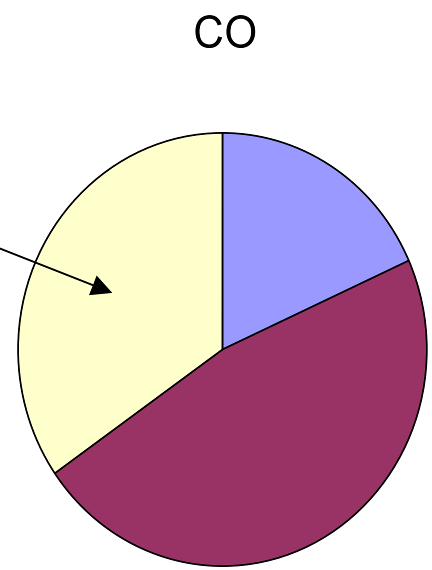
Global assessment of biomass burning and carbon release

Source	burned biomass (Tg dry mass a^{-1}) Dignon (1995)		C release (Tg C a^{-1})	
			Dignon (1995)	Malingreau and Zhuang (1998)
Tropical forest	1230	(1230-2430) [a]	550-1090	570
Savanne	3470	(1190-3690) [a]	540-1660	1660
Boreal forest	520	(280-1620) [a]	130-230	130
Burning wood	1880	(620-1880) [a]	280-850	640
Charcoal	-	(21) [a]	30	30
agricultural waste	1360	(280-2020) [a]	300	910
Tundra	4	(-)	2	-
total	7660	(3625-11665) [a]	1800-4740	3940

[a] Variation after different authors see in Malingreau and Zhuang (1998)

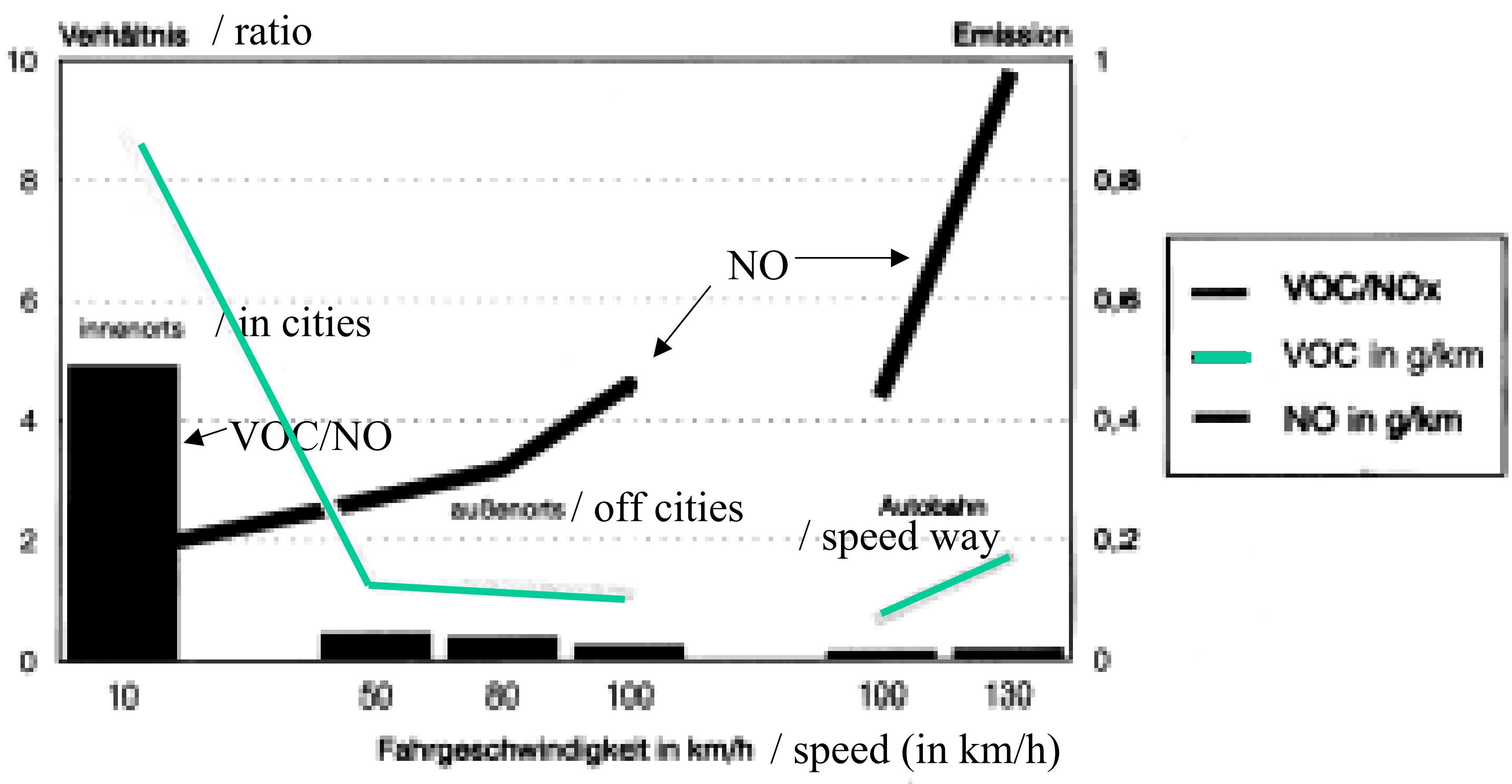
Traffic (fuel burning)





no control, i.e. catalytical converter not yet works!

Light car emission contributions in Germany, after TFS (Friedrich et al.)



Quelle: Hassel et al., 1994 (nach Friedrich 1996)

Yearly gasoline consumption (in l $capita^{-1}$), after IEA (1999)

Region	1987	1997	Country	1987	1997
Northern Amerika	1618	1637	Canada	1660	1688
Australia	970	950	USA	1222	1178
Europe	232	303	Kuwait	803	1309
Near East and North Africa	127	149	Sweden	649	621
South America	122	148	Germany	482	491
Southsaharian Africa	31	31	France	443	334
			Japan	308	422
			South Africa	219	267
			Tschech Republic	137	238
			Poland	104	170
			China	20	35
			Ghana	21	26

Traffic emissions (in mg substance km^{-1} per car), estimated by tunnel experiments (Tauerntunnel, Austria), after Schmid et al. (1998, 2001)

parameter /substance	Thursday	Sunday
number trucks h^{-1}	82	13
number light cars h^{-1}	383	464
mean speed (in km h^{-1})	75	78
CO	2539	1674
CO_2	303000	145000
NO (as NO_2)	3131	788
SO_2	100	39
TVOC (total VOC)	166	193
TC (total carbon)	86	26
NMVOC	165	186
HNO_2	56.3	17
Toluene	16.9	23.0
Benzene	7.9	9.5
m,p-Xylene	12.1	15.8
HCHO (Formaldehyd)	6.9	6.7
CH_3CHO (Acetaldehyd)	2.7	2.3
HCl	< 0.1	< 0.1
HNO_3	1.3	< 0.4
PM	111	44

Emission of NO (in kt N) in Eastern Germany (in 1982), after Möller et al. (1985)

source	emission
power plants	98
traffic	62
high temperature processes	20
house burning (heating)	7
chemical industy	6
total anthropogen	193
soils (agriculture and forestry)	4,4
forest fires	0,1

Global secondary emissions (in Tg a^{-1})

species	Process	secondary emission	primary emission
N-NO	NH_3 oxidation	< 1	70
N-NO	N_2O oxidation	< 1	
C-CO	VOC Oxidation	700-2400	1100
C-CO_2	CO and VOC oxidation	2000-4000 (?)	11000
C-CH_4	NMVOC oxidation	(?)	420
S-SO_2	oxidation of reduced S species	5-20	80
S-COS	CS_2 oxidation	0,6	0.4
S-sulfate	SO_2 oxidation	50	100
PM	*gas-to-particle-conversion*	200	>3000