- EU-Rahmenrichtlinien:
  - EU-Brüssel
  - Grenzwerte für Gesundheit
  - Focus PM 10/2.5, NO_2, O_3
- CAFE: Clean Air For Europe

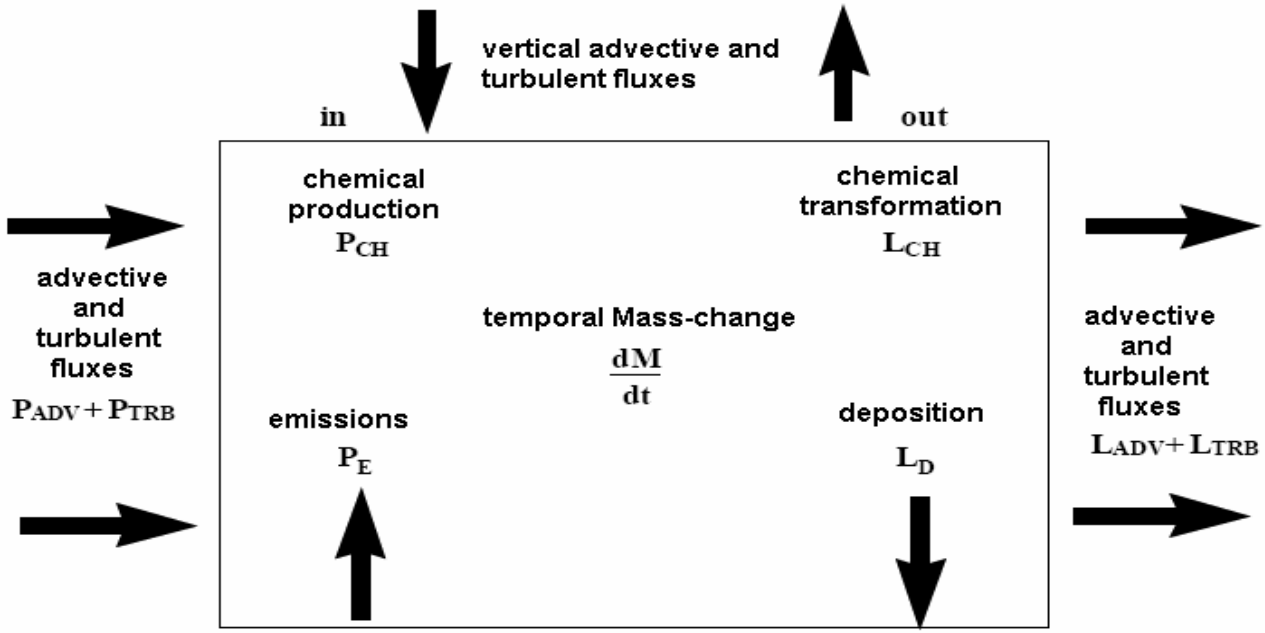
- UN-ECE Convention:
  - Genf
  - Götheborg Protokol
  - NEC-Richtlinien für Öko-system
- EMEP-IIASA

The main problems of the cities seem to be exceedances of daily mean values of PM 10 and annual average of NO_2

Pollutant	Limit value	Averaging time
EU:		
NO_2	40 $\mu gr/m^3$	annual average
	200 $\mu gr/m^3$	1-hour, not to be exceeded more than 18 TPY
PM 10	40 $\mu gr/m^3$	annual average
	50 $\mu gr/m^3$	24-hour, not to be exceeded more than 35 TPY
US:		
NO_2	100 $\mu gr/m^3$	annual average
PM 10	50 $\mu gr/m^3$	annual average
	150 $\mu gr/m^3$	24-hour, not to be exceeded more than 1 TPY
PM 2.5	15 $\mu gr/m^3$	annual average
	65 $\mu gr/m^3$	24-hour (the 3-year average of the 98-percentile of 24-hour conc. not to be exceeded)

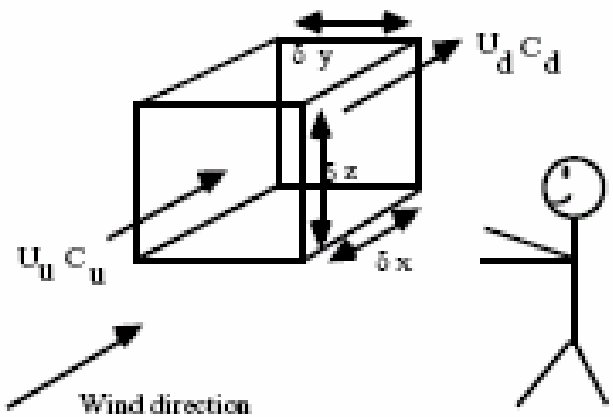
Chemisches Transportmodel

$$\frac{\partial C_i}{\partial t} + \nabla\left[\ (\mathbf{V}C_i - \mathbf{K}\rho\nabla(\frac{1}{\rho}C_i)\ \right] = 0$$

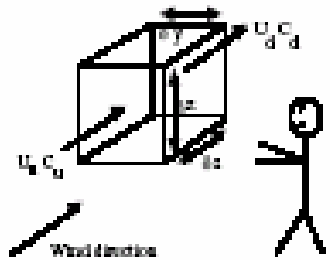


$$\frac{dM}{dt} = (P_{ADV} + P_{TRB} + P_E + P_{CH}) - (L_{ADV} + L_{TRB} + L_D + L_{CH})$$

How do we account for the effects of transport on C?



- **An observer standing at a fixed point in space measures changing concentrations. The observer must account for the chemical sources and sinks as well as for the motion of the air. This is called an Eulerian measurement since it is at a point.**



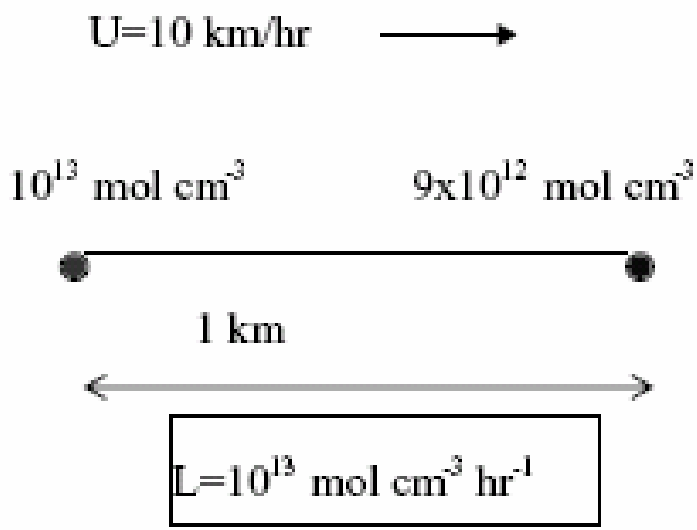
- The flux of material into the upwind side of the box is $U_u C_u$ (particles per cm^2 per sec.)

- The total number of particles being added per second is $U_u C_u dydz$ (particles per second), where dydz is the area of the open face of the box.

- Therefore, considering that material is also leaving the box on the downwind side, the total amount of material added to the box per second, divided by the volume of the box so that we have the particles added cm^{-3} s^{-1}, is

$$\frac{\partial C}{\partial t} = (U_u C_u - U_d C_d) / dx = -dUC / dx$$

Example of flux based Eulerian transport:



- Assume the wind speed is constant at 10 km hr^{-1}.
- Assume the concentration declines by 10^{12} molecules cm^{-3} km^{-1} in the wind direction.
- Assume the concentration declines by 10^{13} molecules cm^{-3} hr^{-1} due to a chemical sink.

The rate of change in the concentration at the fixed downwind position is

$$\frac{\partial C}{\partial t} = -10^{13}\frac{\text{mol}}{\text{hr}} - (10\frac{\text{km}}{\text{hr}})(\frac{9x10^{12} - 10^{13}}{1}\frac{\text{mol}}{\text{km}}) = 0$$

Hence, in this example the advection by the wind completely masks the ongoing chemical loss of the material.

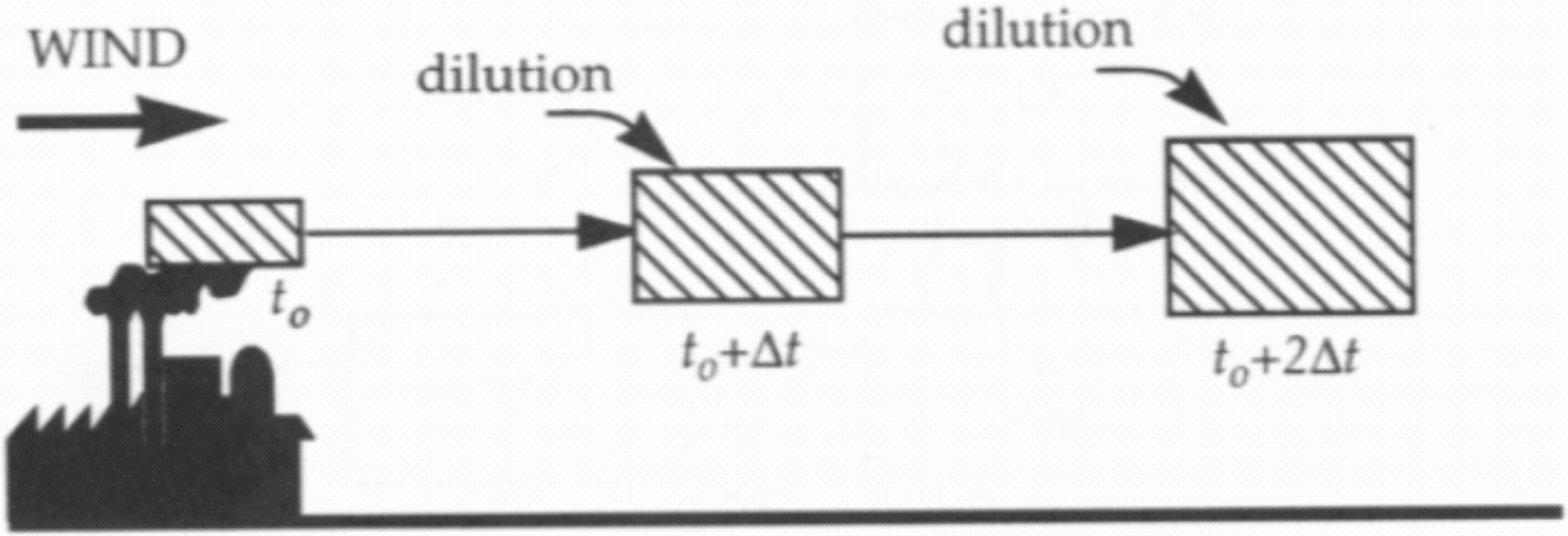
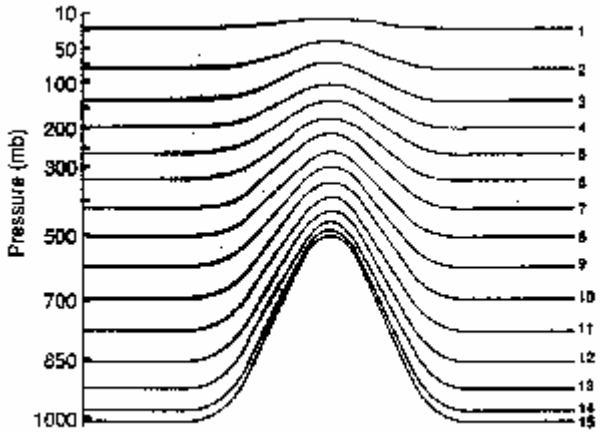
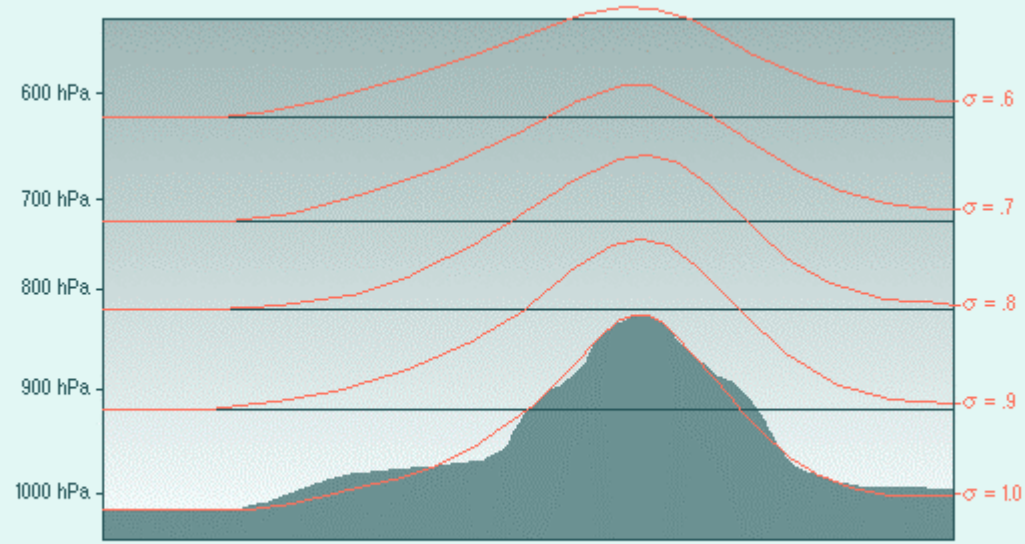


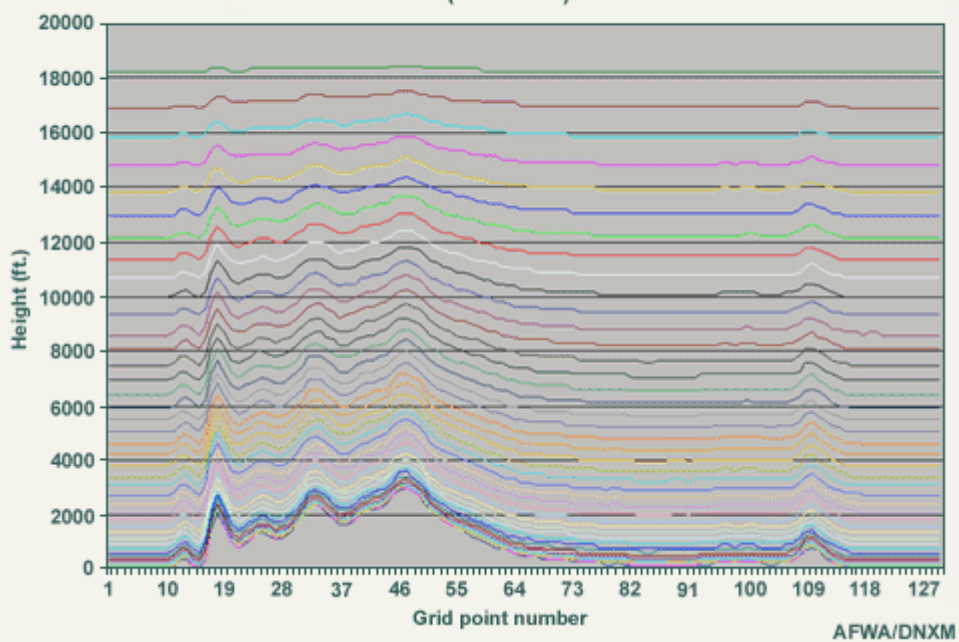
Fig. 3-7 Puff model for a pollution plume.

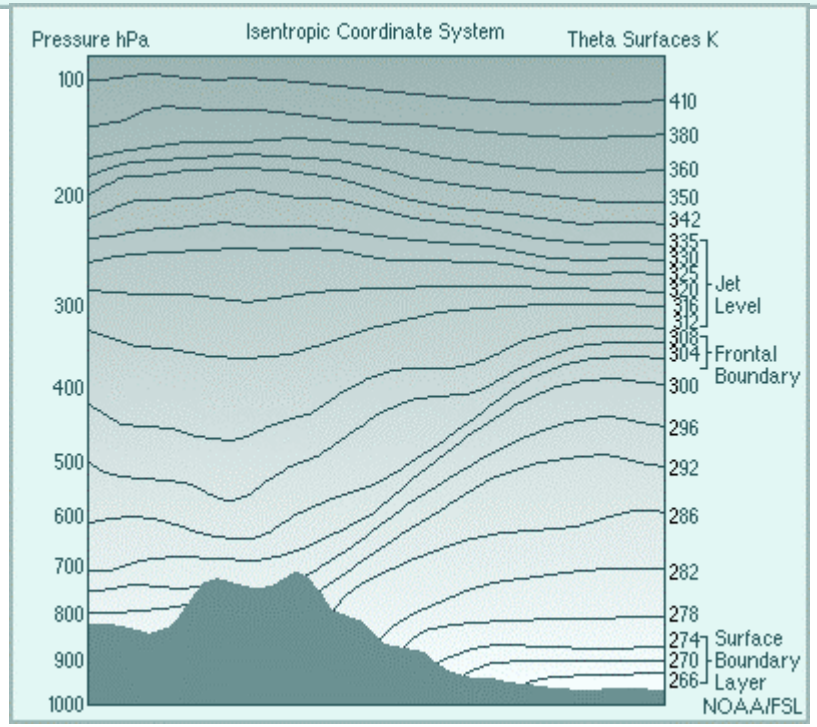


15 livelli in coordinate sigma

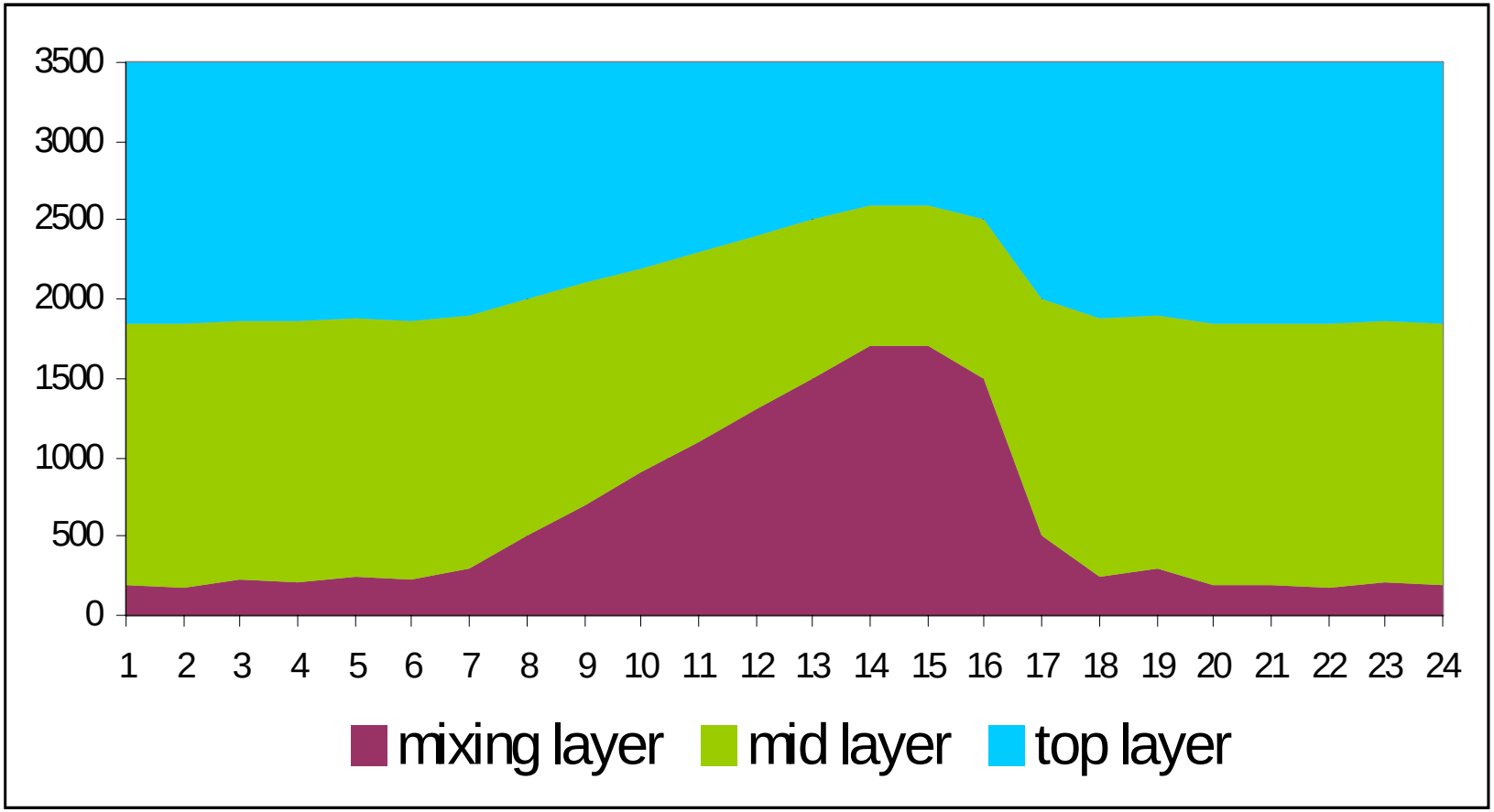


The COMET Program





Vertikalkoordinate



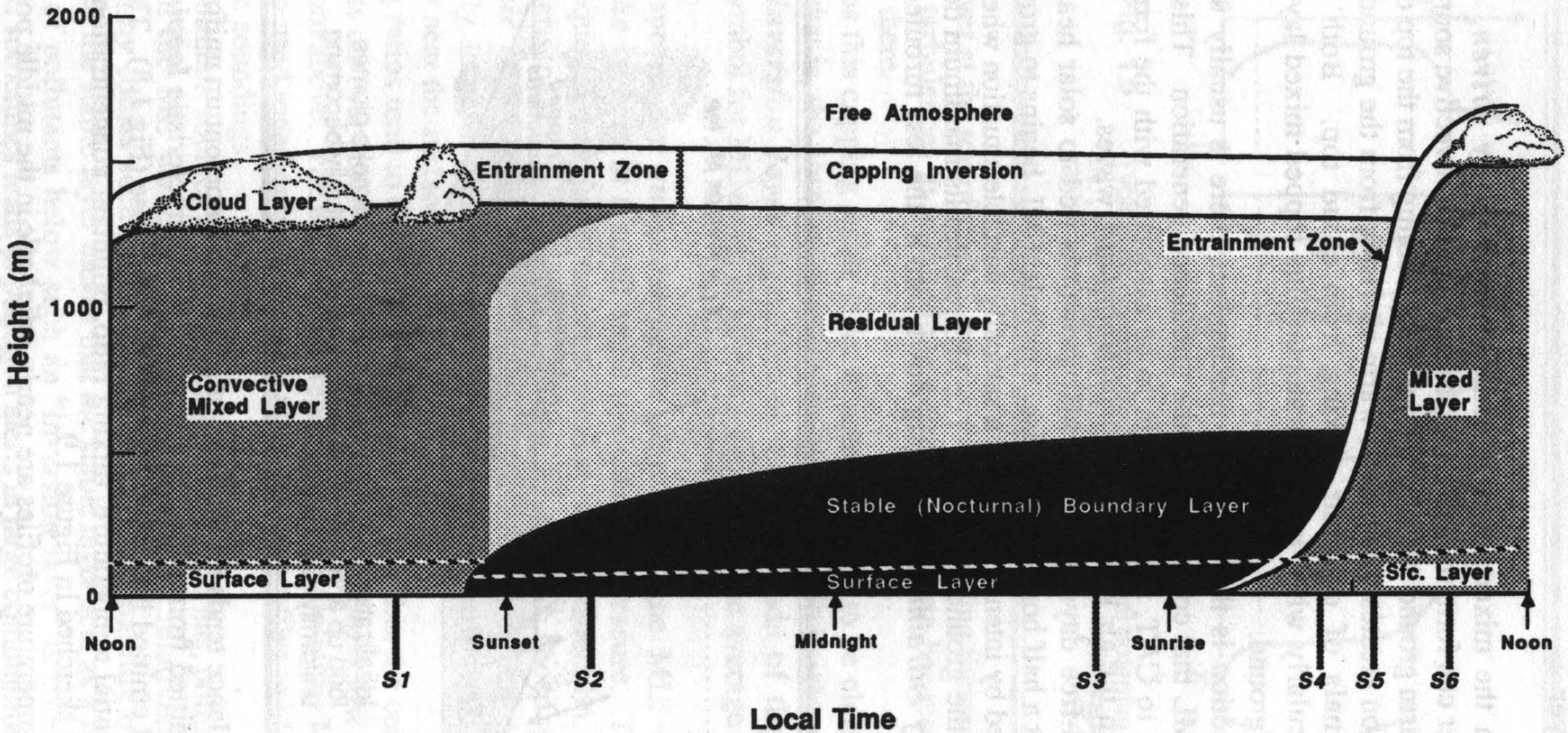


Fig. 1.7 The boundary layer in high pressure regions over land consists of three major parts: a very turbulent mixed layer; a less-turbulent residual layer containing former mixed-layer air; and a nocturnal stable boundary layer of sporadic turbulence. The mixed layer can be subdivided into a cloud layer and a subcloud layer. Time markers indicated by S1-S6 will be used in Fig. 1.12.

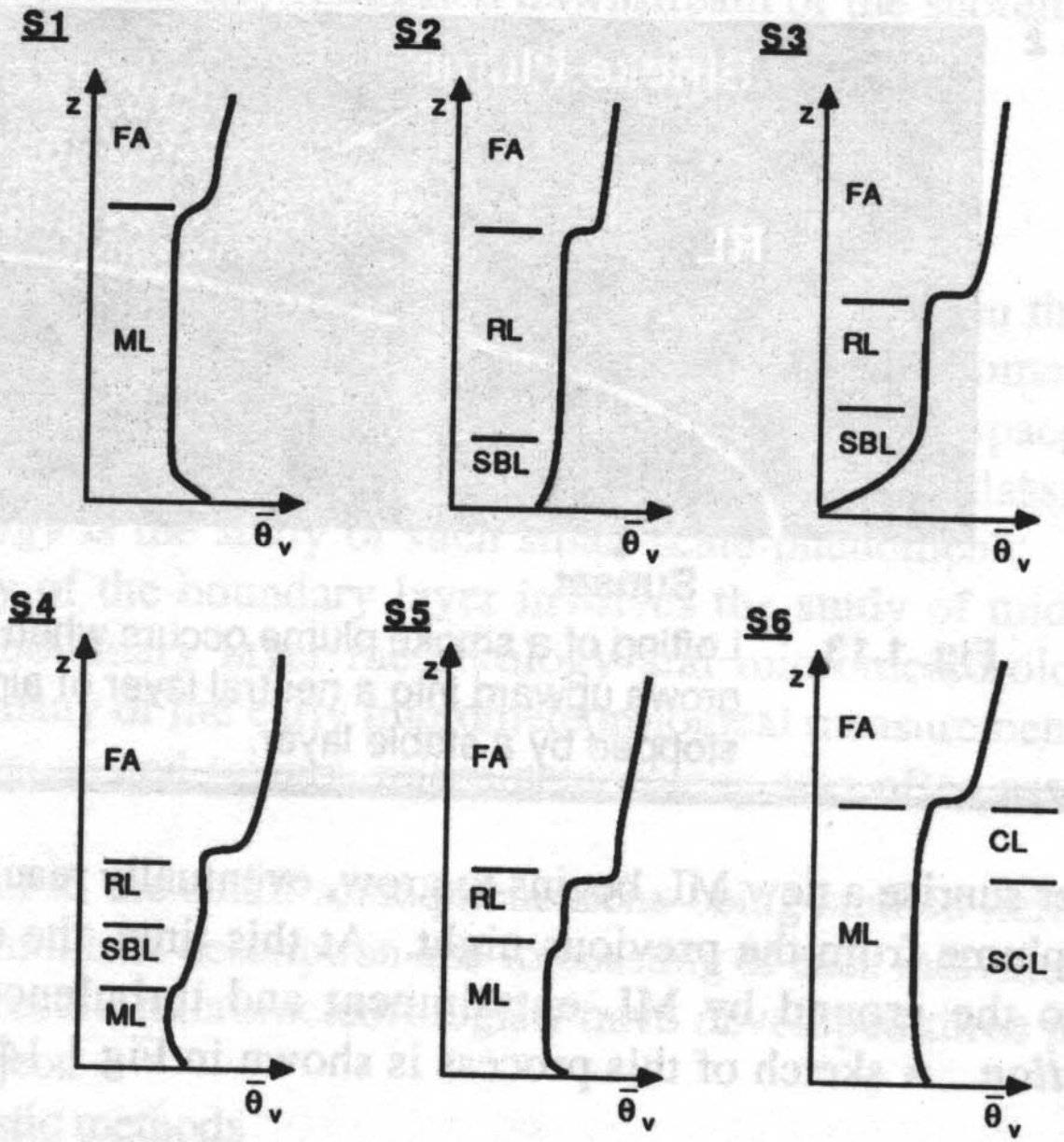


Fig. 1.12
Profiles of mean virtual potential temperature, $\bar{\theta}_v$, showing the boundary evolution during a diurnal cycle starting at about 1600 local time. S1-S6 identify each sounding with an associated launch time indicated in Fig. 1.7.

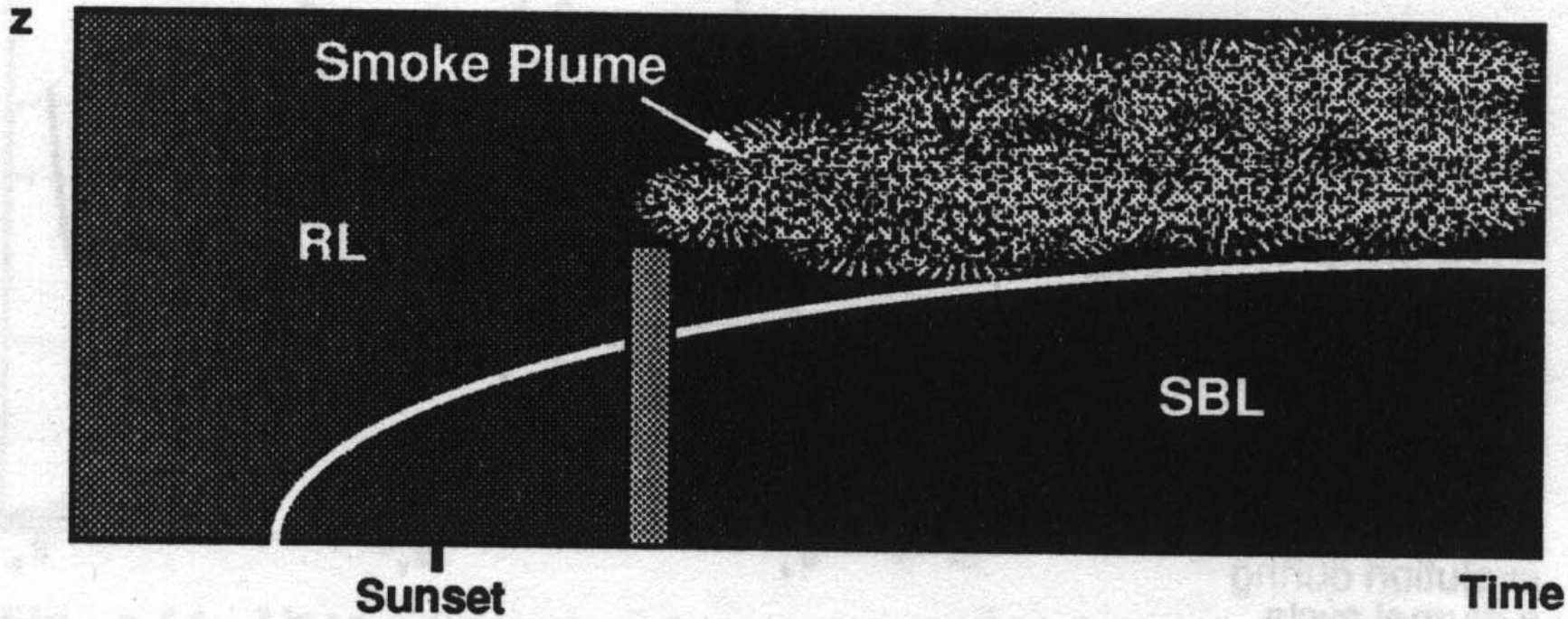


Fig. 1.13 Lofting of a smoke plume occurs when the top of the plume grows upward into a neutral layer of air while the bottom is stopped by a stable layer.

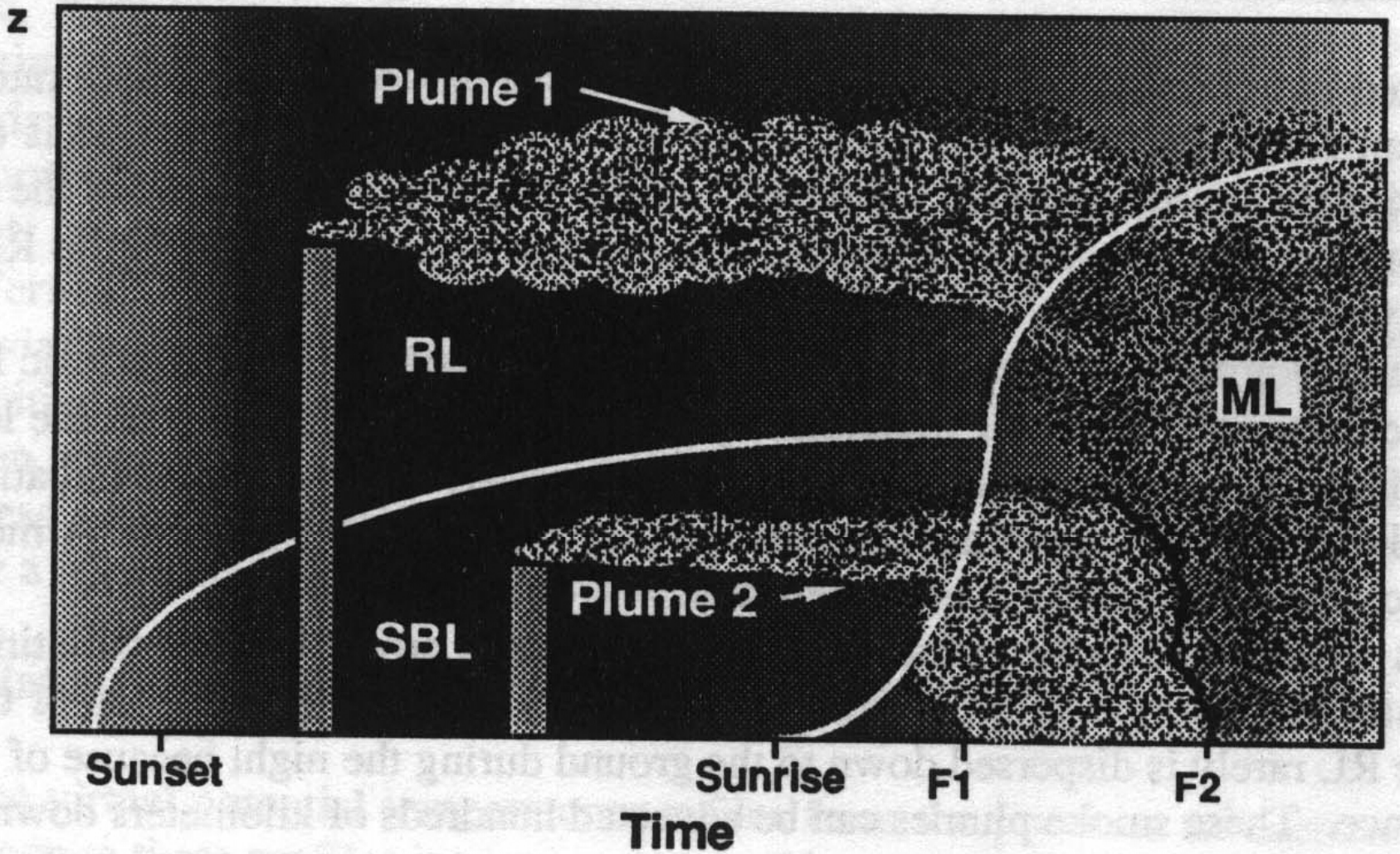


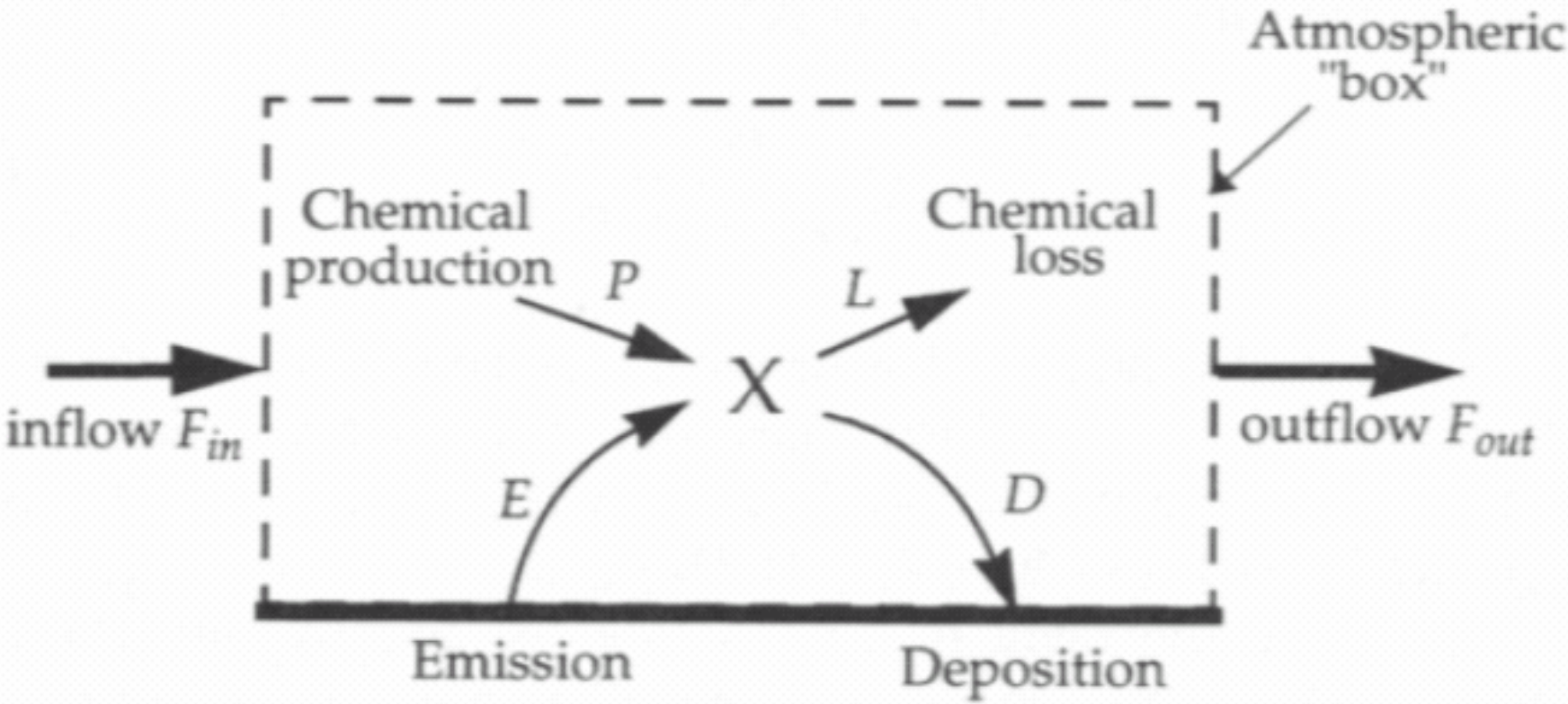
Fig. 1.14 Sketch of the fumigation process, where a growing mixed layer mixes elevated smoke plumes down to the ground. Smoke plume 1 is fumigated at time F1, while plume 2 is fumigated at time F2.

The basis of atmospheric transport-chemistry modelling

$$\frac{\partial C_i}{\partial t} + u\frac{\partial C_i}{\partial x} + v\frac{\partial C_i}{\partial y} + w\frac{\partial C_i}{\partial z} = \frac{\partial}{\partial x}\left(K_h \frac{\partial C_i}{\partial x}\right) +$$

$$\frac{\partial}{\partial y}\left(K_h \frac{\partial C_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial C_i}{\partial z}\right) +$$

chemistry + emissions – dry deposition – wet deposition


Atmospheric "box"
Chemical production
P
L
Chemical loss
X
inflow F_{in}
outflow F_{out}
E
D
Emission
Deposition

Tropospheric chemistry

- Gasphase chemistry: tropospheric ozone and related components
- Heterogeneous chemistry: Aerosol physics and chemistry
- Dry and wet deposition
- Chemical Transport Modelling - CTM
- Emissions

IV. Tropospheric chemistry

Stratospheric chemistry: mostly gasphase

Tropospheric chemistry: gasphase, aquous phase, aerosols

Formation of tropospheric ozone

$$NO_2 + hV \rightarrow NO + O \qquad \lambda < 410\ nm$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

$$NO_2 + O_2 \rightleftarrows NO + O_3$$

Photo-stationairy state

Increase of tropospheric ozone: shift in photo-stationairy state:

$$NO_2 + O_2 \rightleftarrows NO + O_3$$

Reactive hydrocarbons:

$$RH + OH + O_2 \rightarrow RO_2 + H_2O$$

$$RO_2 + NO \rightarrow RO + NO_2$$

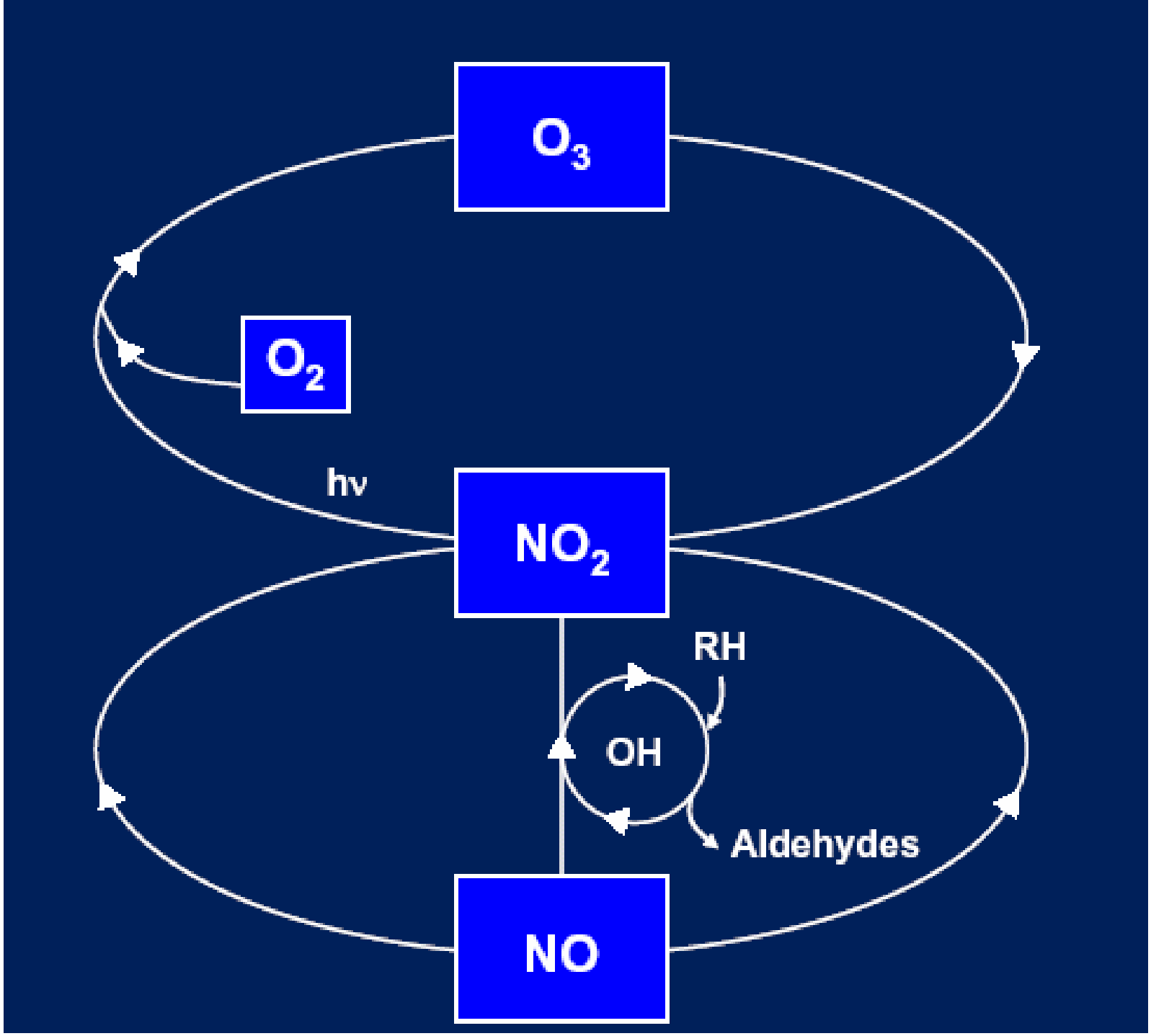
R: CH_3, C_2H_5 etc. etc.

$$RO + O_2 \rightarrow \text{Aldehydes} + HO_2$$

$$H_2O + NO \rightarrow NO_2 + OH$$

Reactive Hydrocarbons: RH's transform NO in NO_2 without a loss of O_3, so leads to increase in O_3 concentration

Different RH's have a different Photochemical Ozone Creation Potential: POCP


O_3
O_2
hν
NO_2
RH
OH
Aldehydes
NO

Policy for tropospheric O_3

RH versus NO_x abatement,

Non-lineair: $NO + O_3 \rightleftarrows NO_2 + O_2$

lowering of NO leads to increase in O_3

high RH/NO_x-ratio: NO_x-strategy

low RH/NO_x-ratio: RH-strategy

Biogenic RH-emissions

Tropospheric O_3-budget

A. Inflow from the stratosphere

B. Dry deposition at the surface

C. Chemical production

D. Chemical destruction

No wet deposition, O_3 does not desolves in water

Aerosols, fine particles, particle matter

Definition:

Dispersed system containing solid or liquid particles suspended in air (cloud droplets are not considered to be aerosols)

Aerosols : Size-spectrum
Chemical composition

Aerosols : Radius > radius molecules
Mass > mass molecules

Aerosols : $> 10^{-3}$ μm

IV) Messungen von Aerosolen

- **Zusammensetzung:**
  - primär, anthropogen und natürlich
  - sekundär anorganisch
  - sekundär organisch-biogen und anthropogen

PM 10 und PM 2.5

- **Chemie sekundärer Aerosole**
- **Anzahl Messungen + Zusammensetzung sehr gering**
  - AFO-2000 Projekt FU-Berlin-Reimer
  - Messungen Stadt Berlin-Lutz

Secondary inorganic aerosol

$NO_2 + OH \rightarrow HNO_3$

$HNO_3 + NH_3 \leftrightarrow NH_4\,NO_3$

$SO_2 + 2OH \rightarrow H_2SO_4$

$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2\,SO_4$

secondary organic aerosol

$$\begin{array}{ccccc} ROG & + & OH & \rightarrow & \Sigma\,\alpha_i\,C_i \\ & + & NO_3 & & \\ & + & O_3 & & \end{array}$$

Soot (Russ) is the same as Black Carbon – BC- or Elementary Carbon-EC

It is produced by burning, so is part of the primary emissions of PM

PM 2.5 exists to a large extent of BC and Organic Carbon-OC

BC might be the health relevant part of PM 2.5

BC is a greenhouse "gas", it absorbs light

Calculation of PM10 Mass in RCG

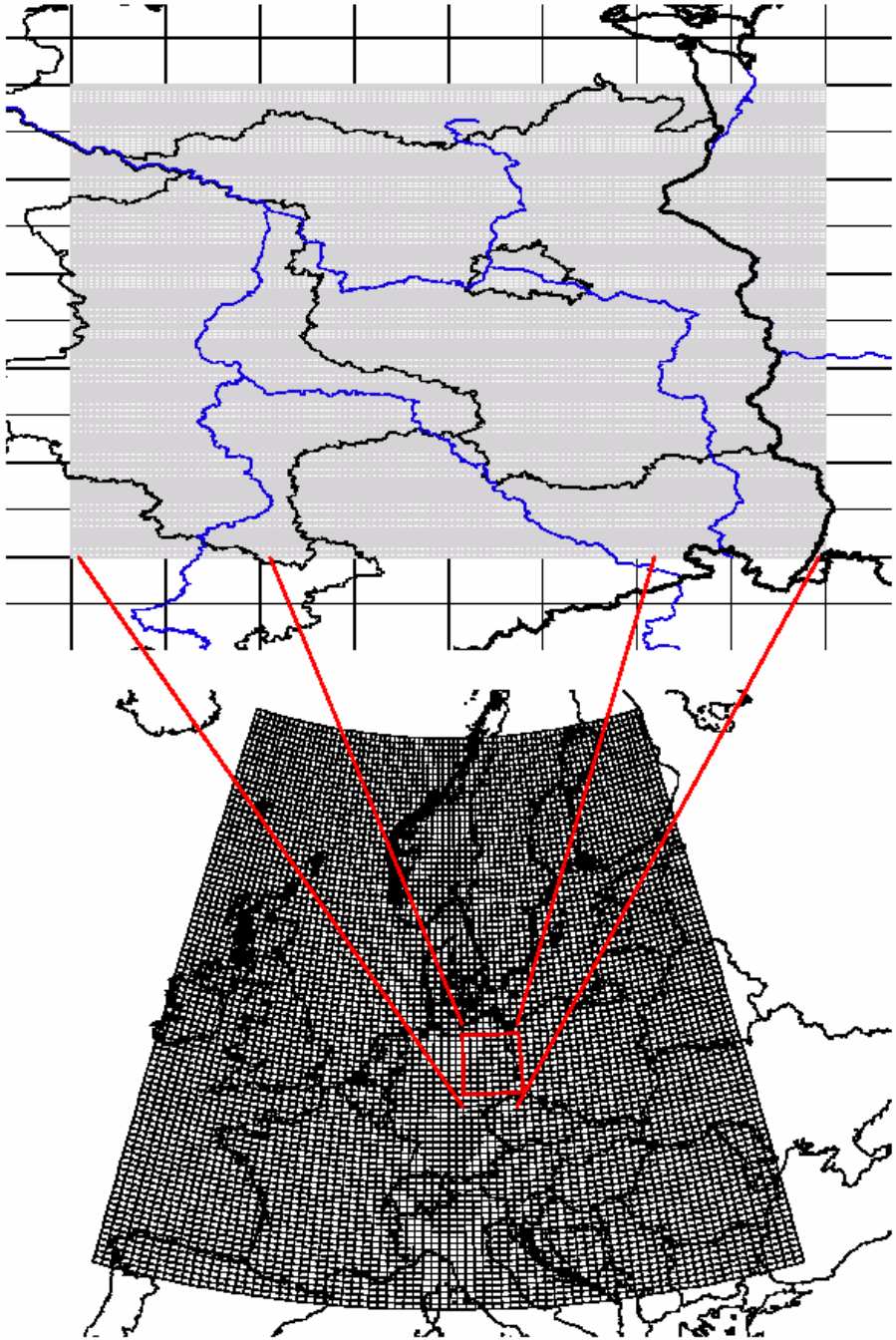
- **Anthropogenic PM emissions are splitted up between fine and coarse**
- **mode and allocated to 4 primary model species: EC, OC, $PM25_{MD}$, $PMCO_{MD}$**

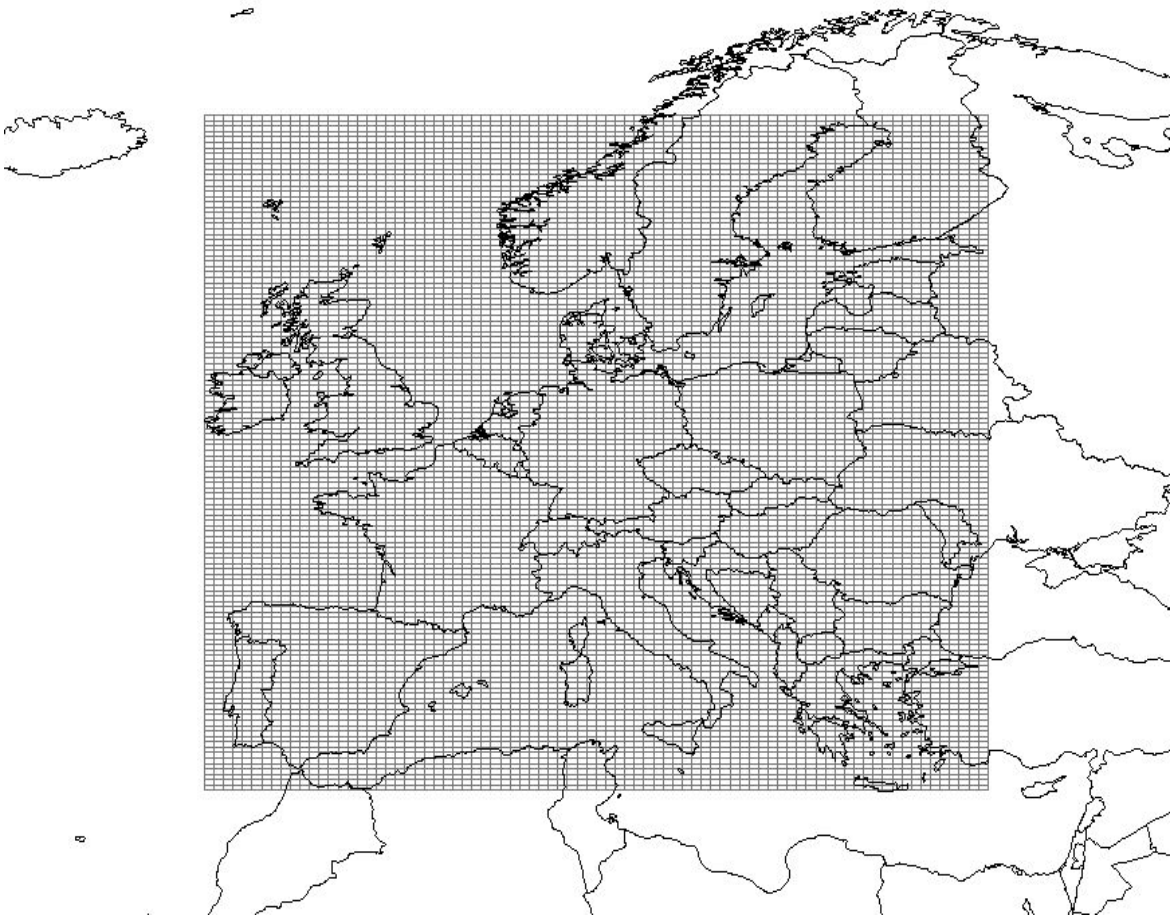
- **All secondary aerosols (3 SIA and 5 SOA) are assigned to the PM2.5 fraction (fine mode)**

- **Wind blown dust is allocated to the primary model species $PM25_{WBD}$, $PMCO_{WBD}$**

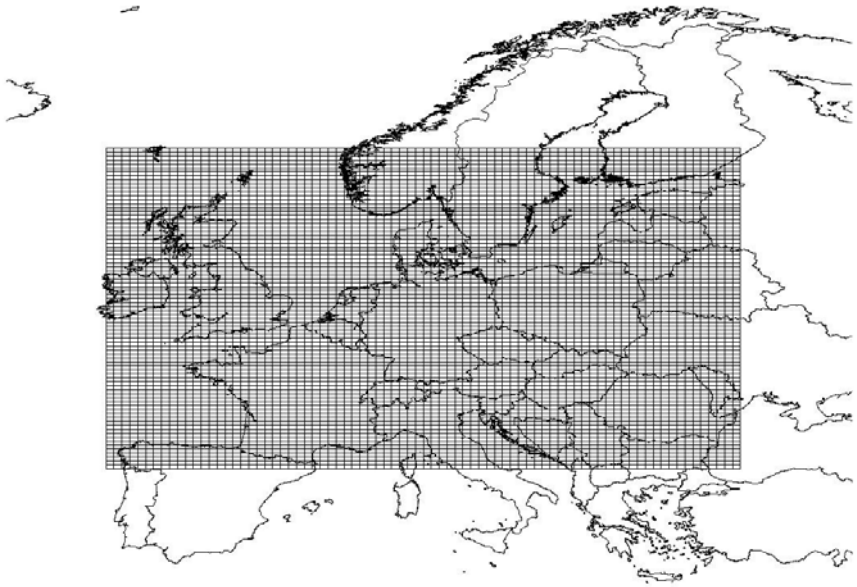
- **Sea salt is assigned to the coarse mode model species Na and Cl**
- Total PM10 mass is sum of 16 species:

  EC + OC + PM25 +PMCO + SIA + SOA+ Na + Cl

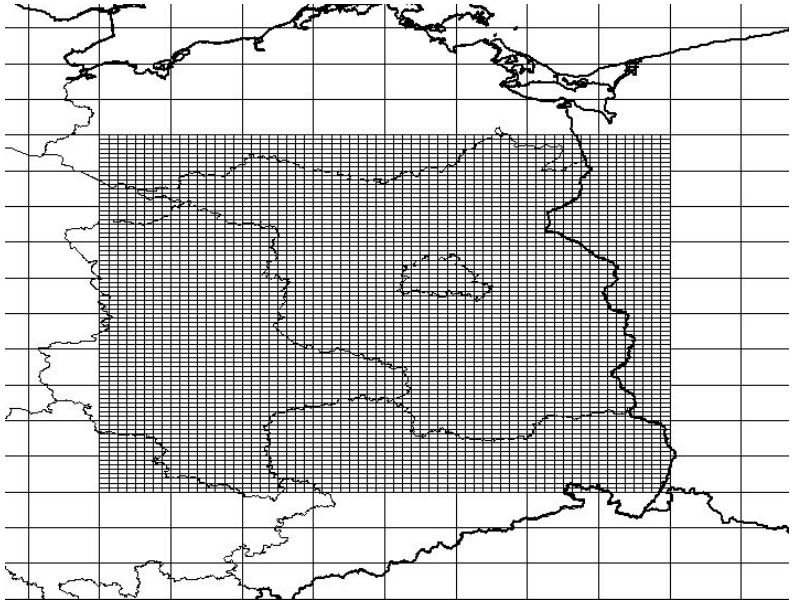


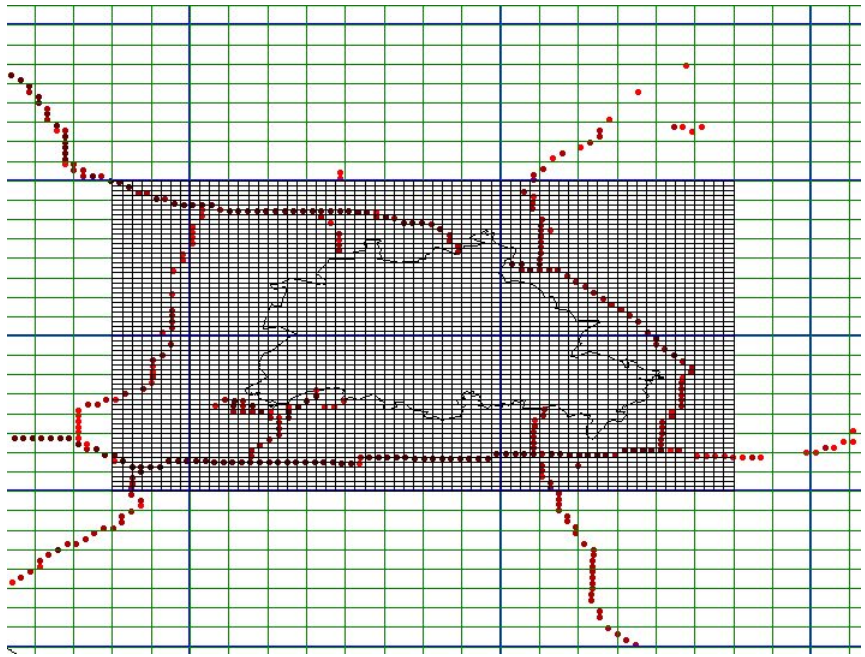


- Resolution: 0.25° Lat, 0.5°
- Long
- 82 x 125 grid cells
- 5 layers up to 3000m
-
- 2 dynamic layers below MH
-
- 2 dynamic layers above MH
- 1 fixed surface layer of 20m



Berlin-Anwendung 2002
Europaweit 25x25 km2
Nest 1 : 4x4 km2
Nest 2 : 1x1 km2



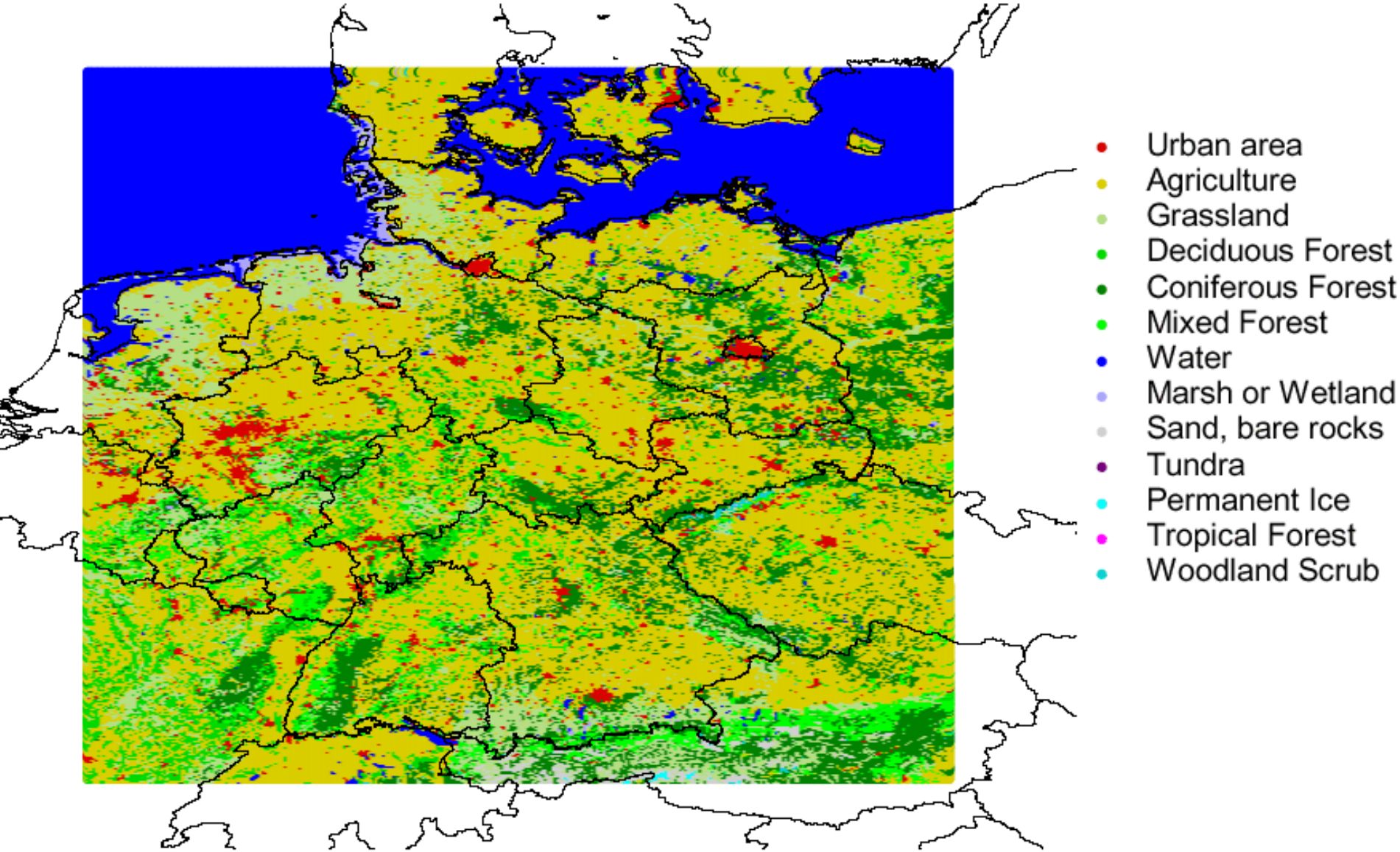


Land Cover

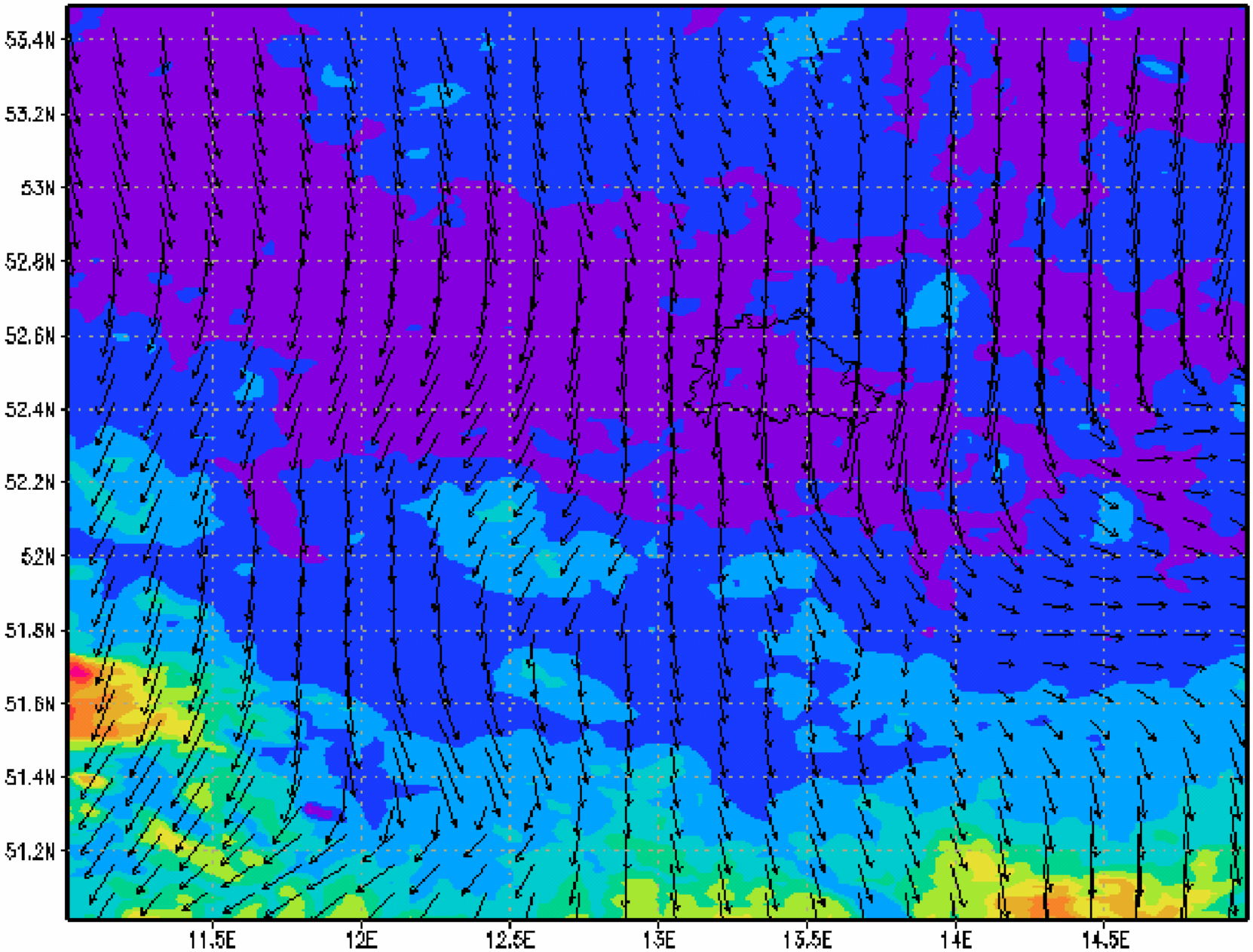
- Urban area
- Arable land
- Irrigated arable land
- Permanent crops
- Pastures
- Natural grassland
- Shrubs and herbs
- Coniferous forest
- Mixed forest
- Deciduous forest
- Bare soil
- Permanent ice and snow
- Wetlands
- Inland water
- Sea
- Out of scope

sc-dlo

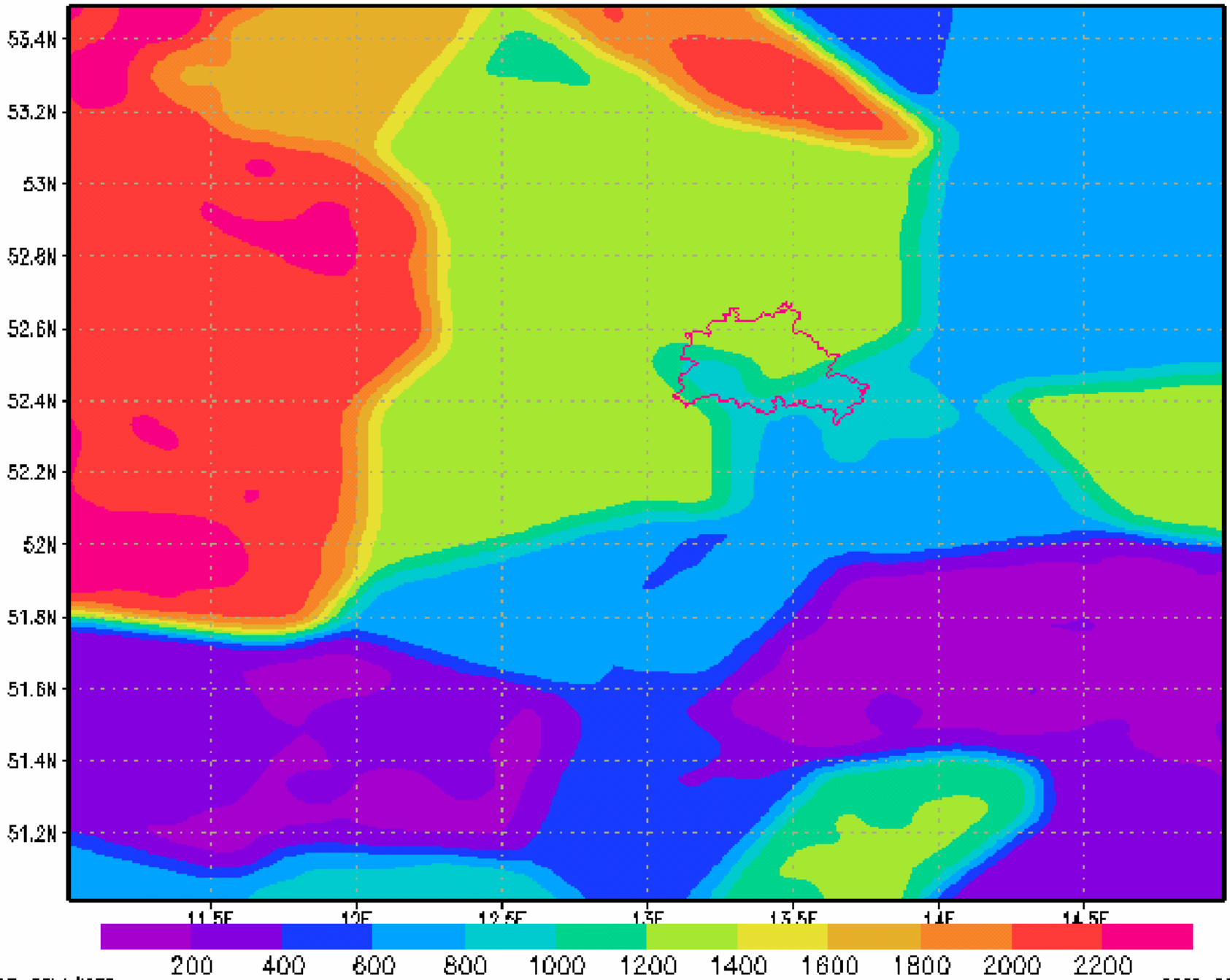
RESOURCE ANALYSIS


Urban area
Agriculture
Grassland
Deciduous Forest
Coniferous Forest
Mixed Forest
Water
Marsh or Wetland
Sand, bare rocks
Tundra
Permanent Ice
Tropical Forest
Woodland Scrub

Windfield at surface [m/s] 15 June 1999 15:00



mixing height 15 June 1999 15:00



CORINAIR SNAP Code

DESCRIPTION

01 Public power, cogeneration and district heating plants

02 Commercial, institutional and residential com-bustion

03 Industrial combustion and processes with combustion

04 Non-combustion production processes

05 Extraction and distribution of fossil fuels

06 Solvent use

07 Road transport

07a Road transport gasoline

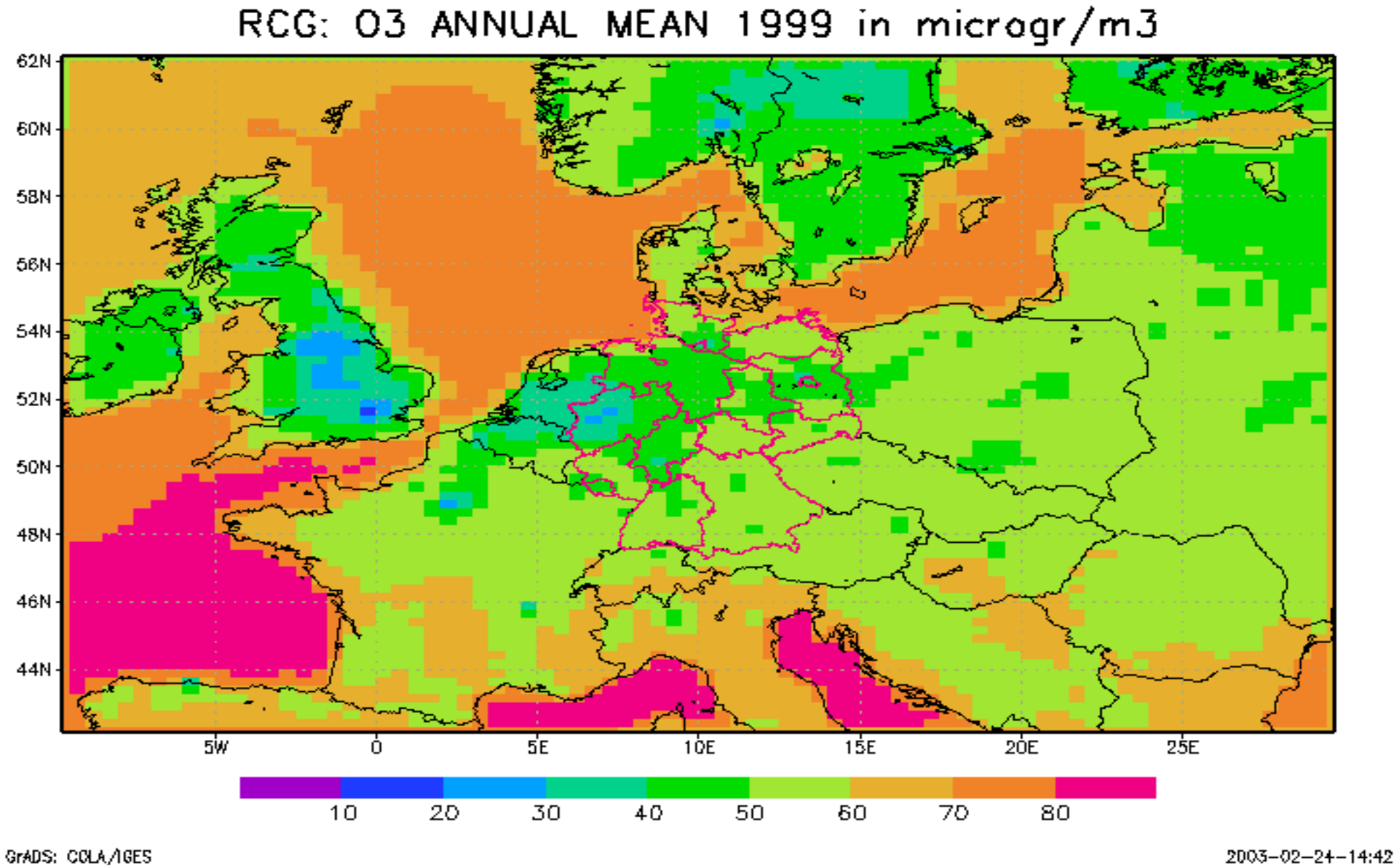
07b Road transport diesel

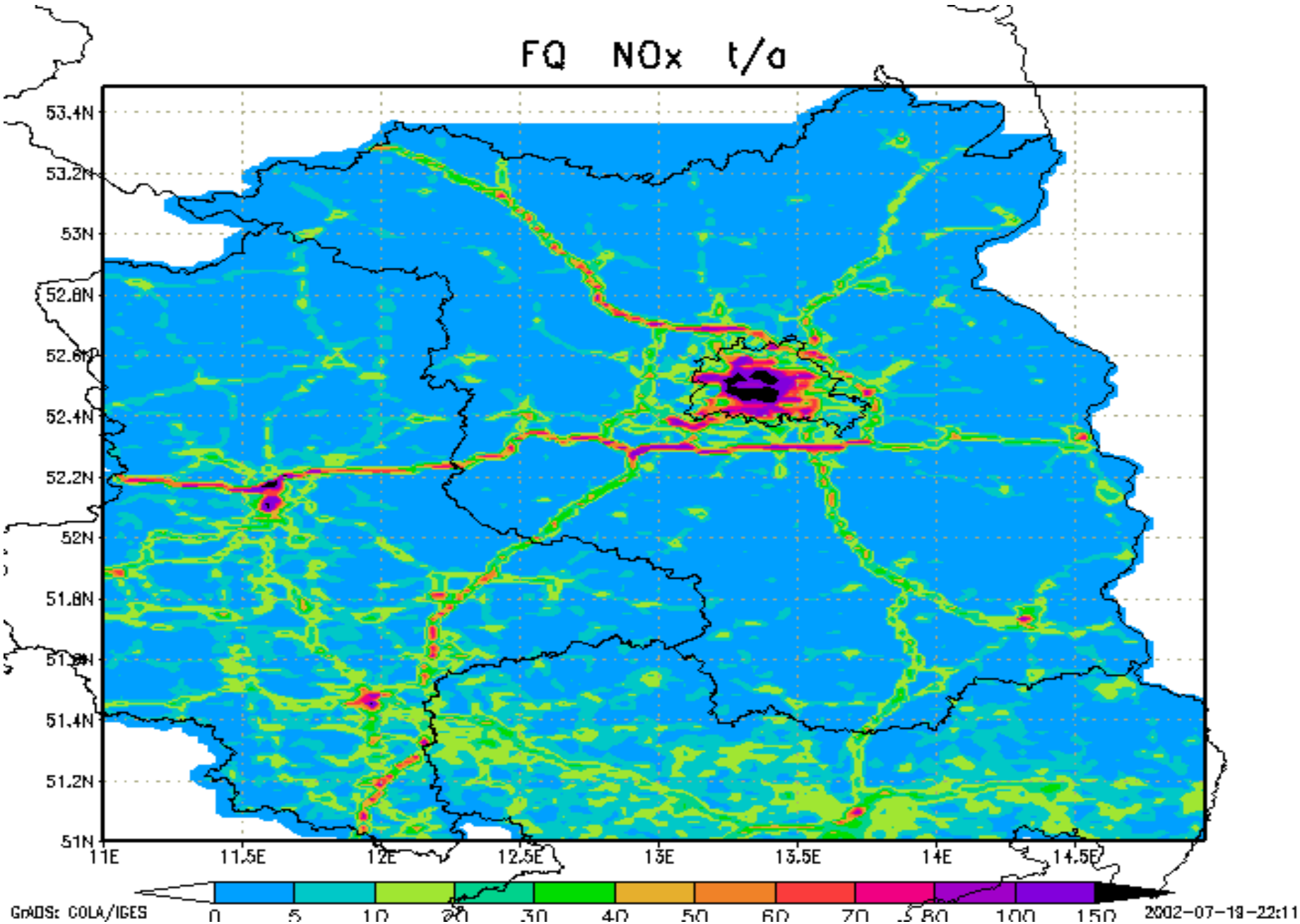
07c Road transport evaporation

08 Other mobile sources and machinery

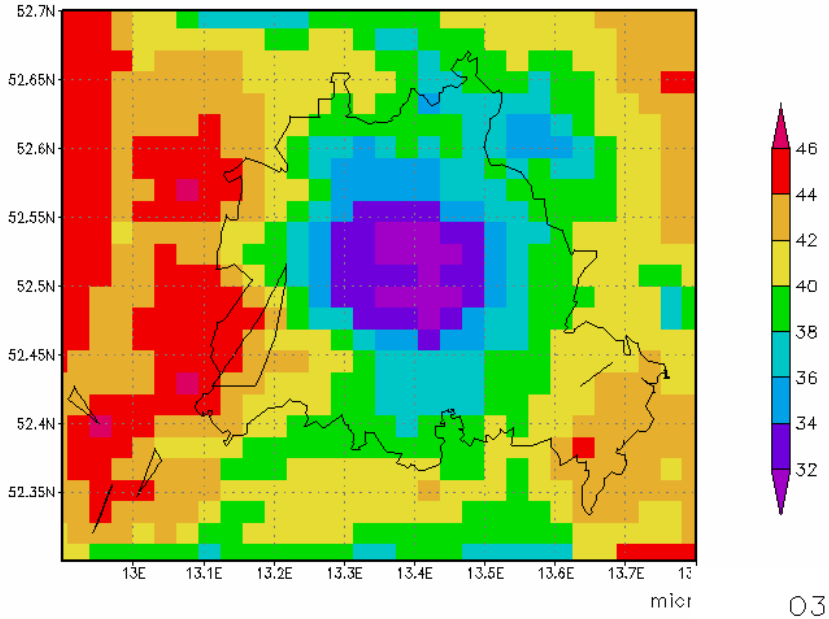
09 Waste treatment and disposal

10 Agriculture


RCG: O3 ANNUAL MEAN 1999 in microgr/m3
62N
60N
58N
56N
54N
52N
50N
48N
46N
44N
5W
0
5E
10E
15E
20E
25E
10
20
30
40
50
60
70
80
GrADS: COLA/IGES
2003-02-24-14:42

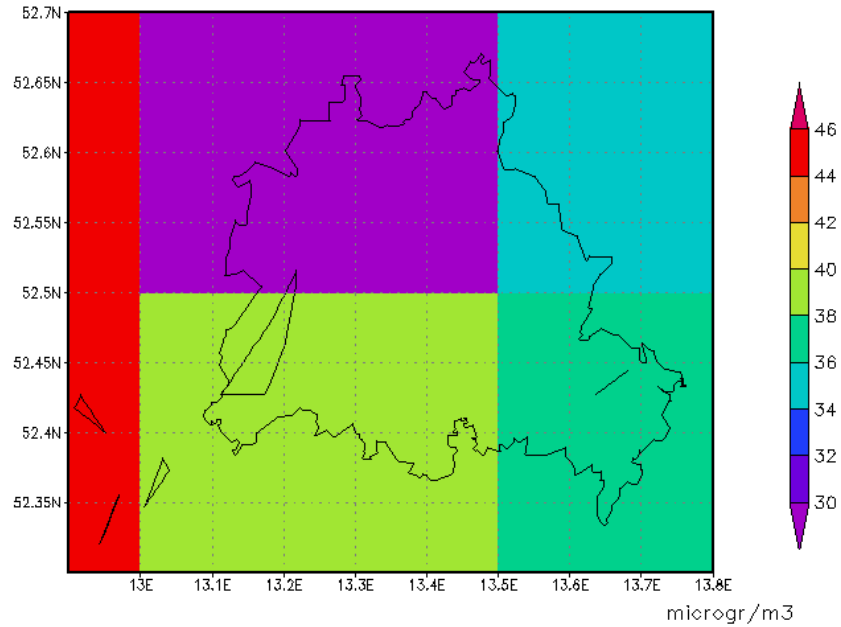

FQ NOx t/a
53.4N
53.2N
53N
52.8N
52.6N
52.4N
52.2N
52N
51.8N
51.6N
51.4N
51.2N
51N
11E
11.5E
12E
12.5E
13E
13.5E
14E
14.5E
0
5
10
20
30
40
50
60
70
80
100
150
GrADS: COLA/IGES
2002-07-19-22:11

O3 Mean in simulation period



FU-Berlin/TrUmF/UBA year 1999 RCG_CONC_96X128_BASE_O3_01.eug

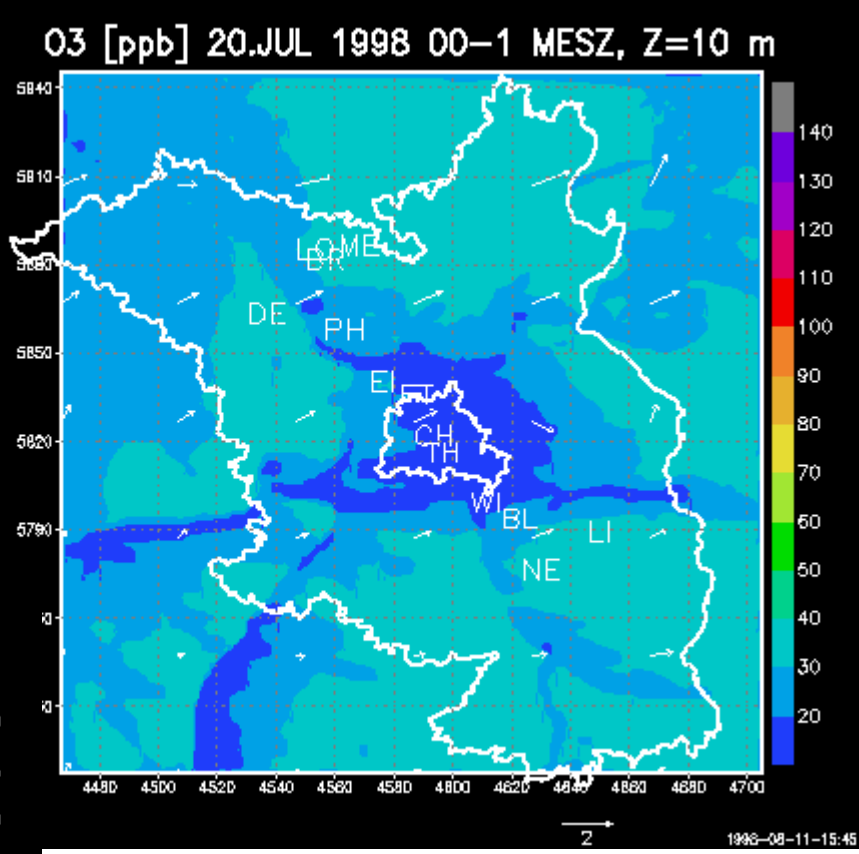
O3 Mean in simulation period



FU-Berlin/TrUmF/UBA year 1999 RCG_CONC_JAHR_1999_CBM_4L_BASE96X128_O3_01.eug

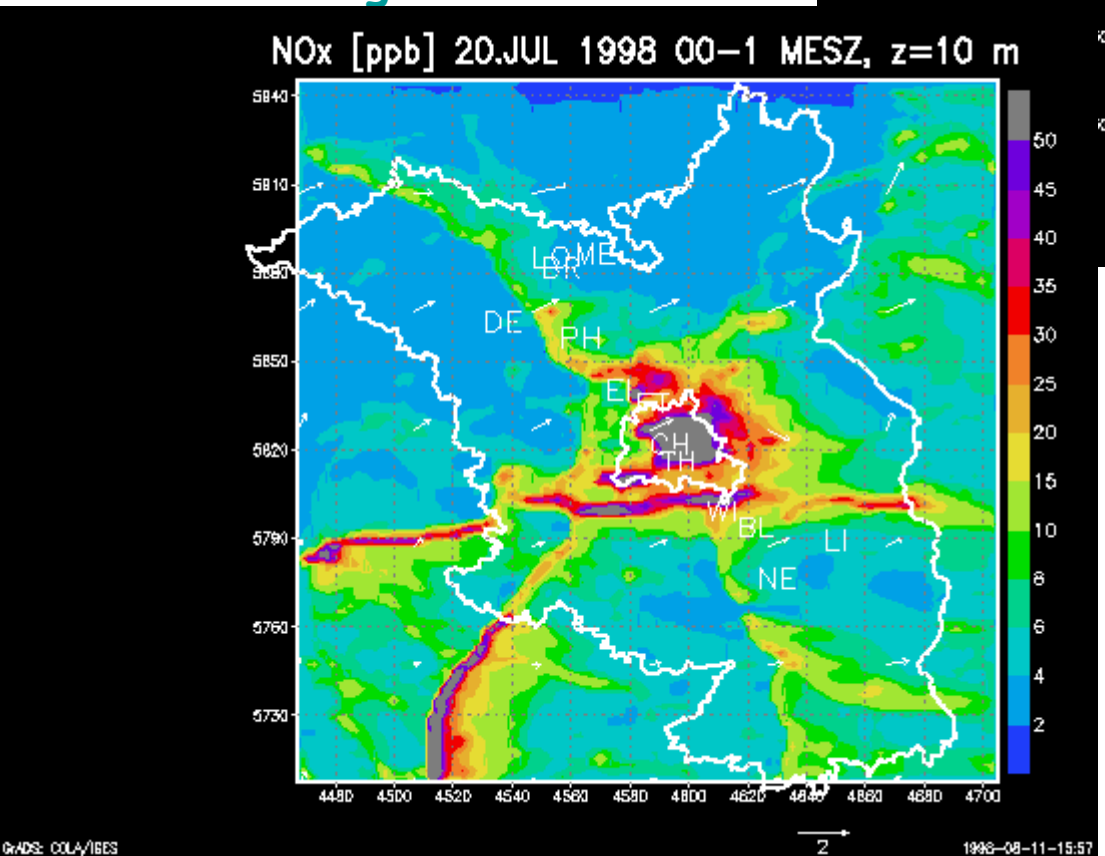
BERLIN PLUME

BERLIOZ episode (jule 1998)



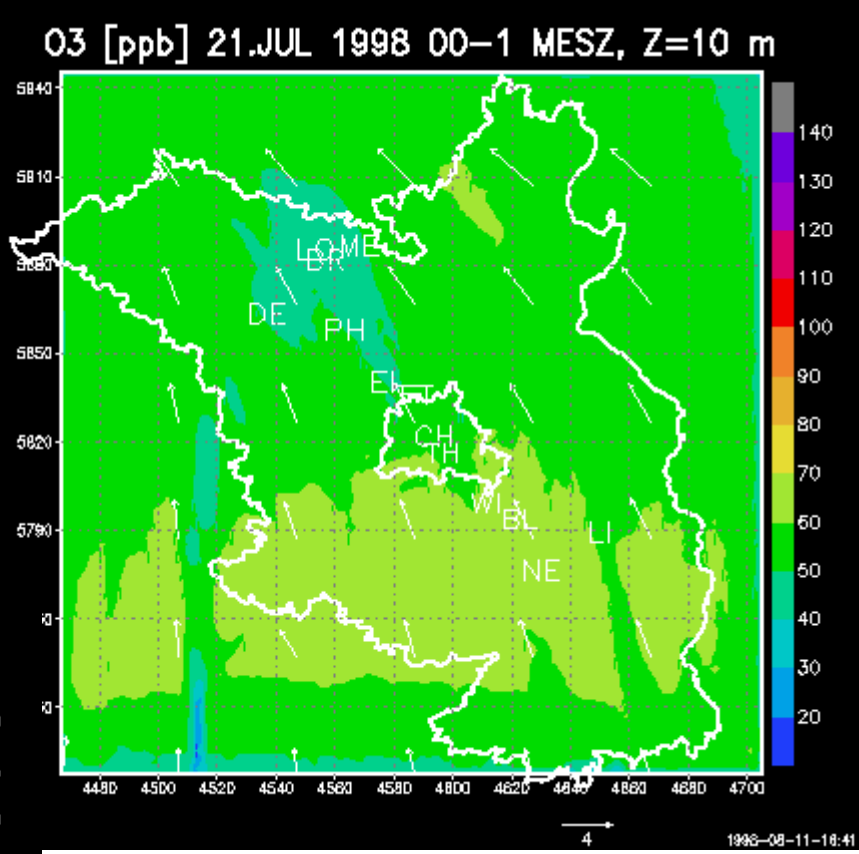
ozone

nitrogen oxides



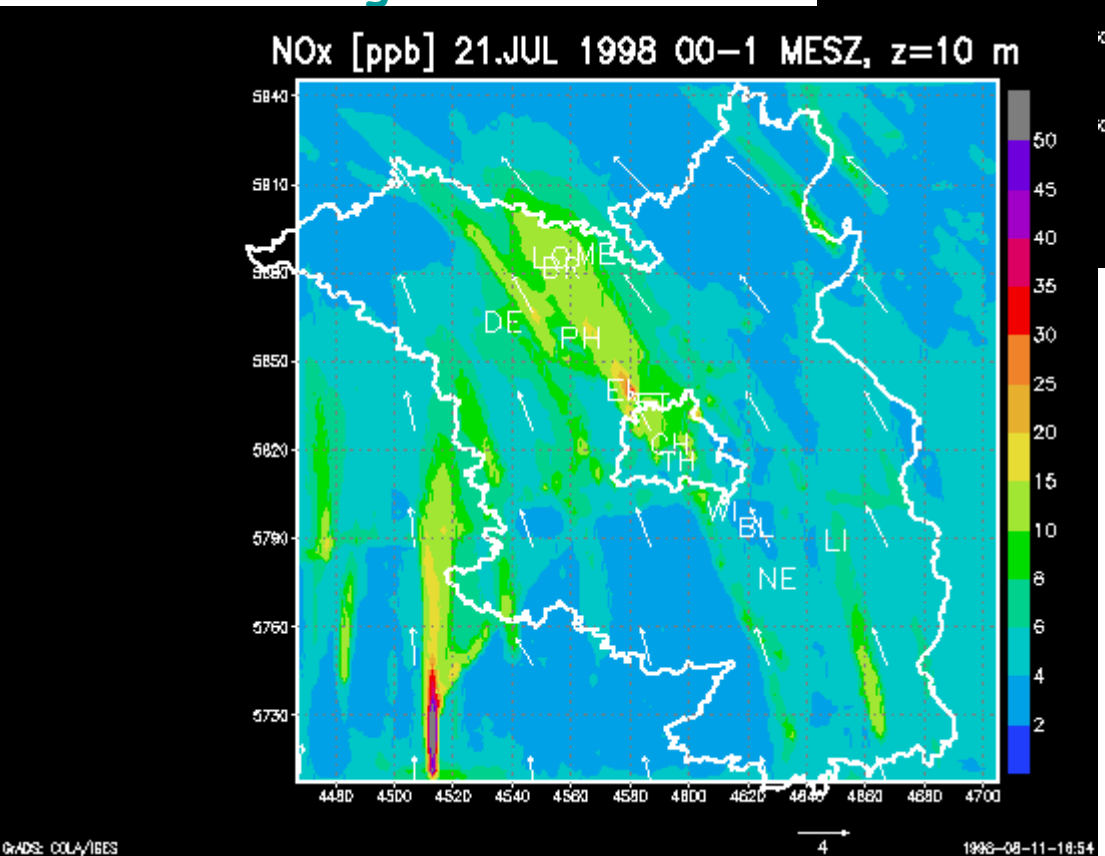
BERLIN PLUME

BERLIOZ episode (jule 1998)



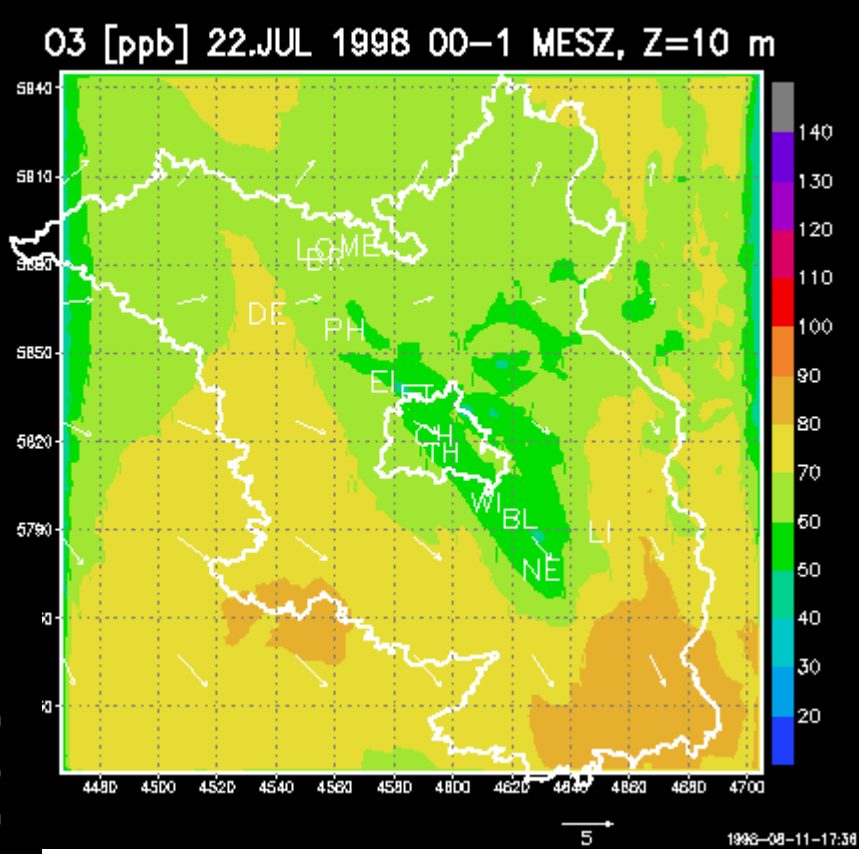
ozone

nitrogen oxides

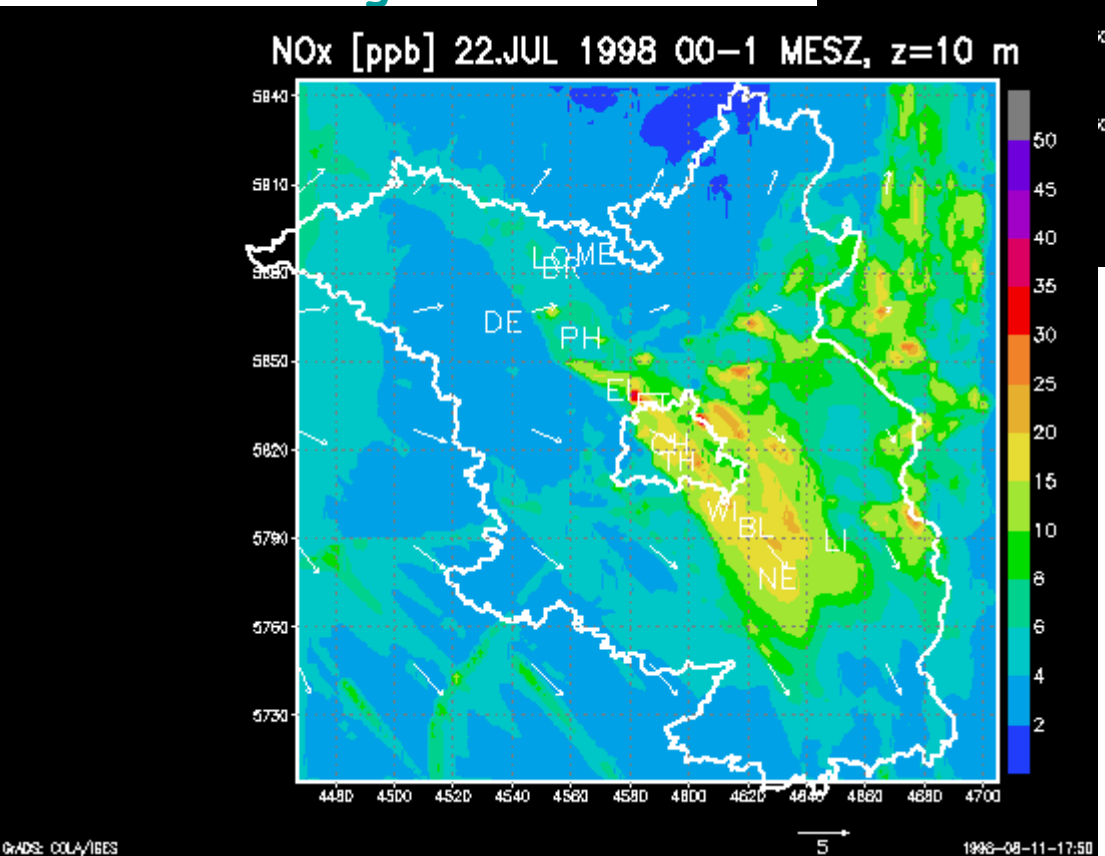


BERLIN PLUME

BERLIOZ episode (jule 1998)



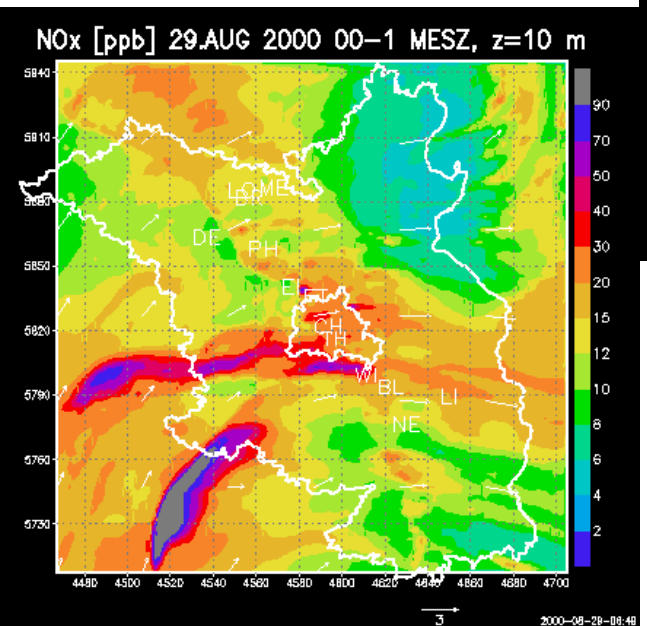
nitrogen oxides

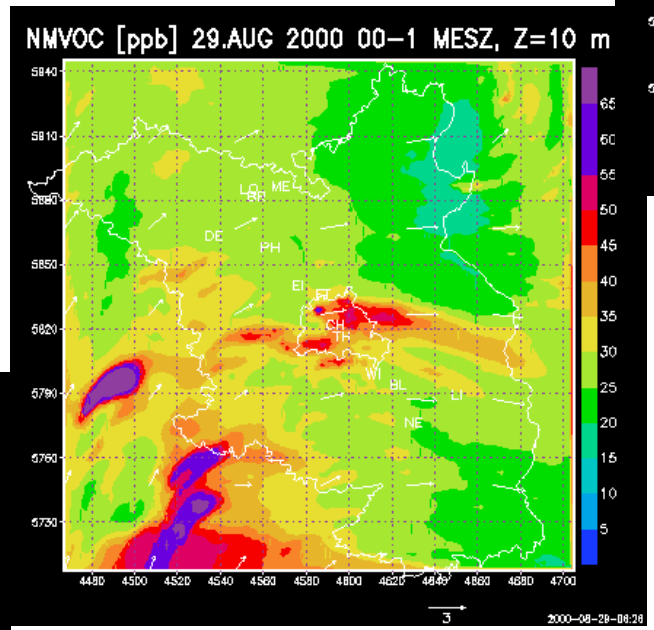


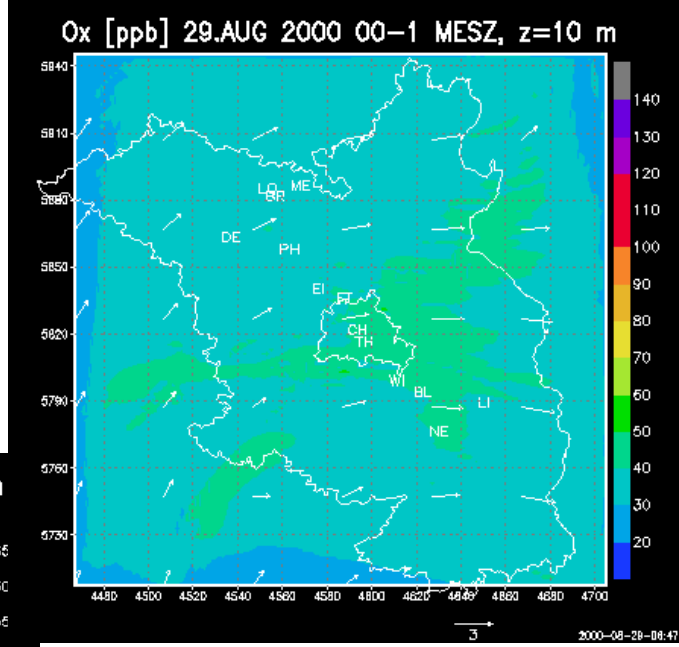
ozone

BERLIN PLUME

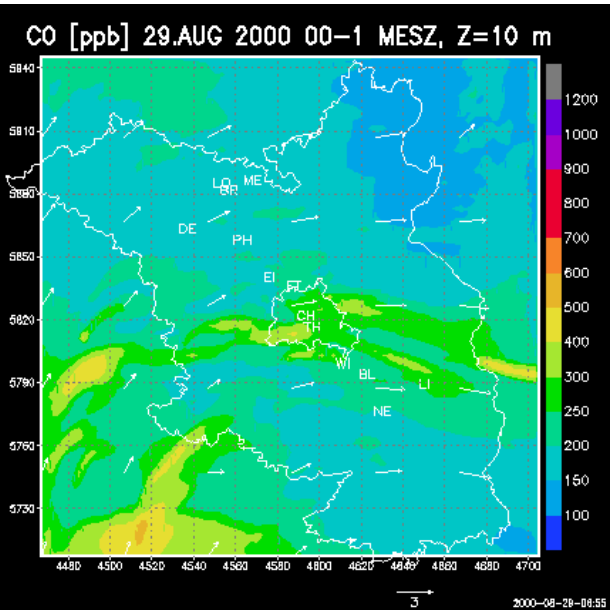
AUG 2000

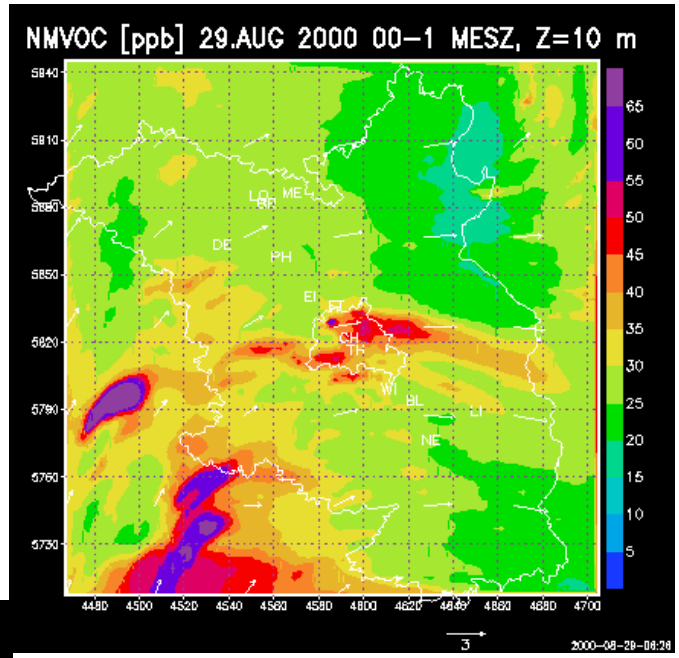


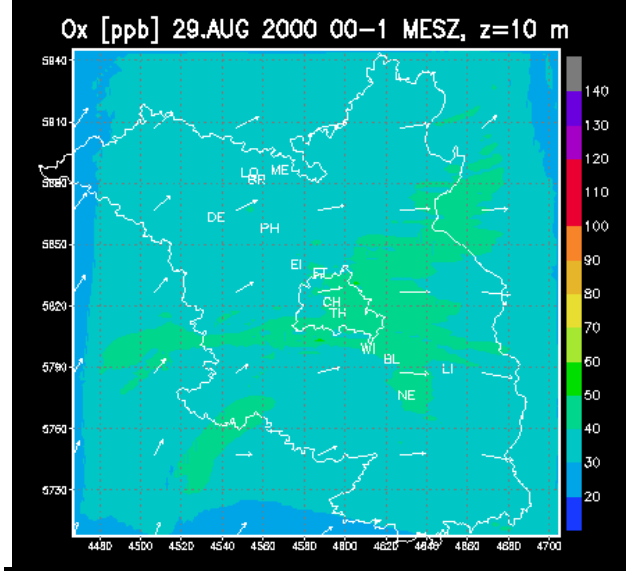


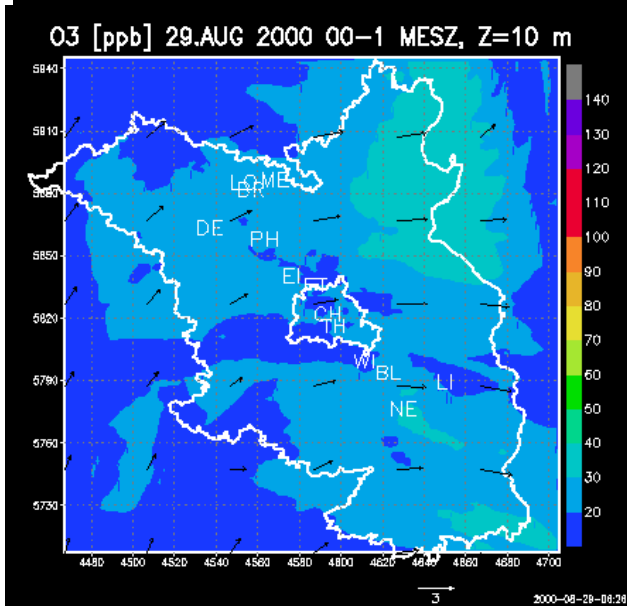


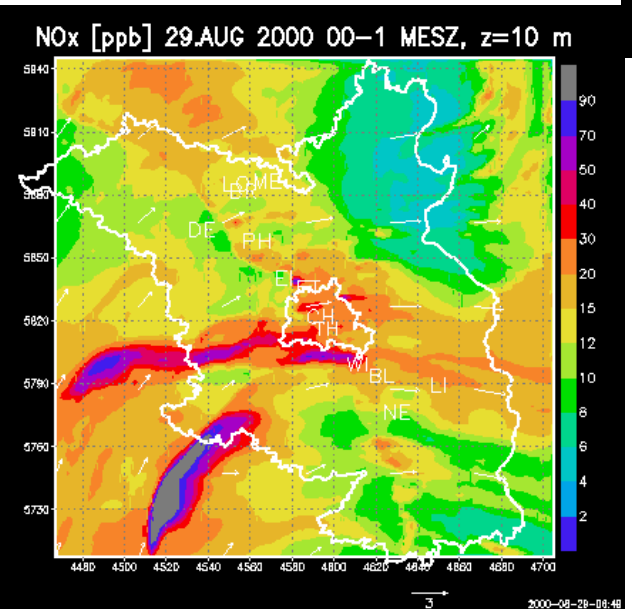
Oxidants AUG 2000

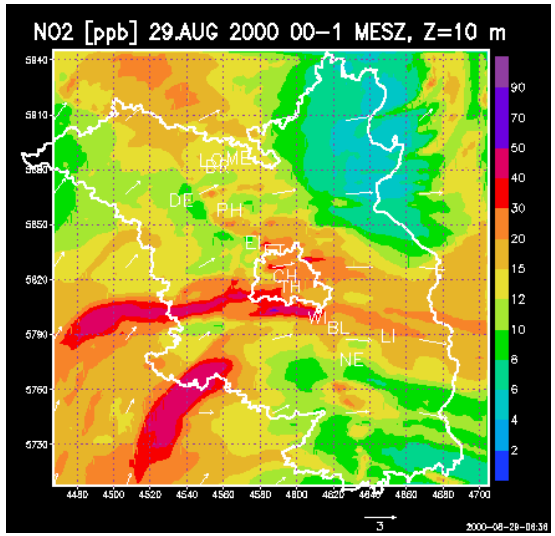












Long Range Modeling

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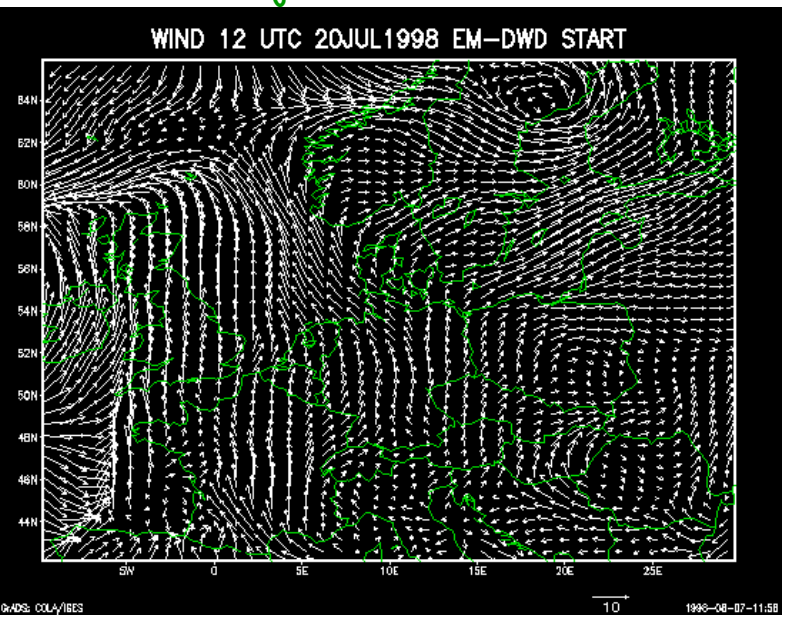
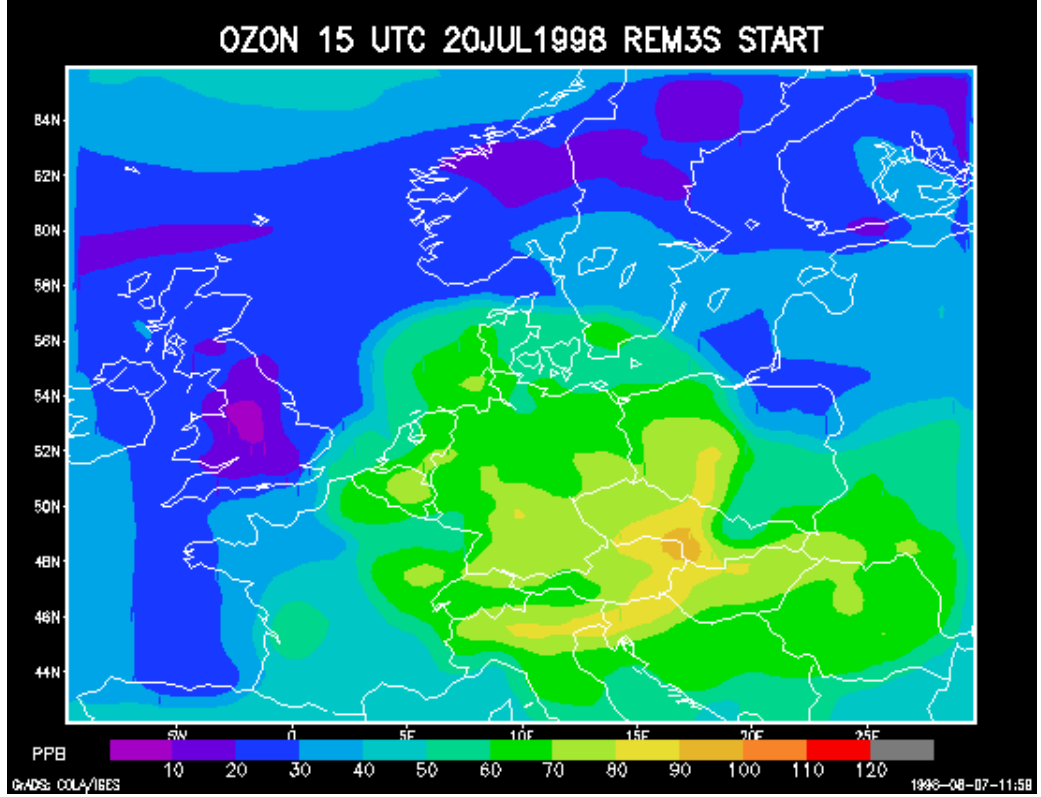
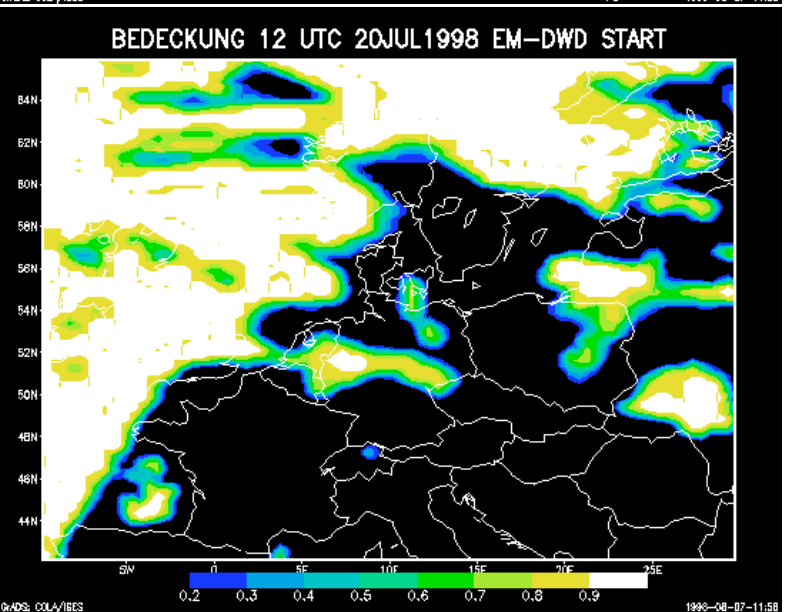
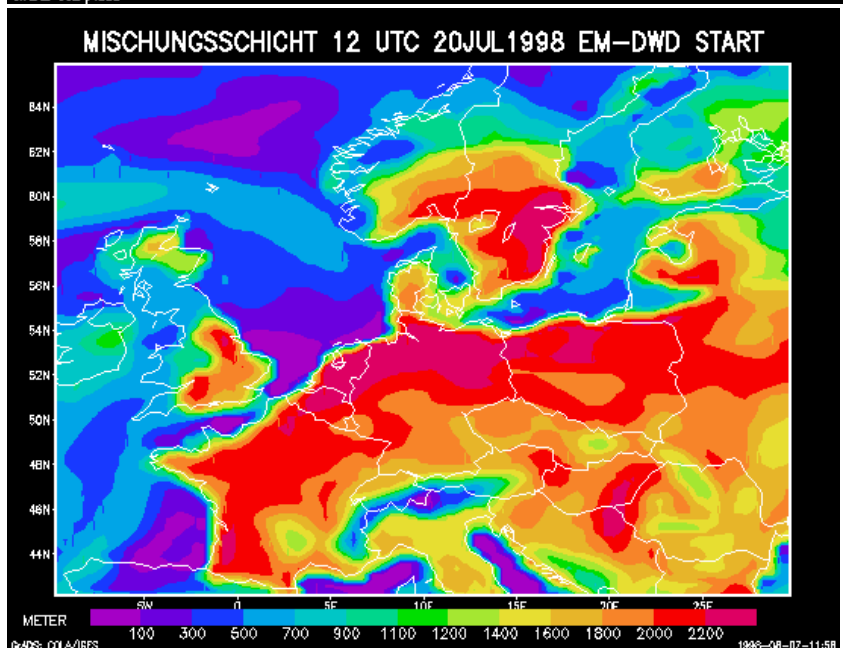
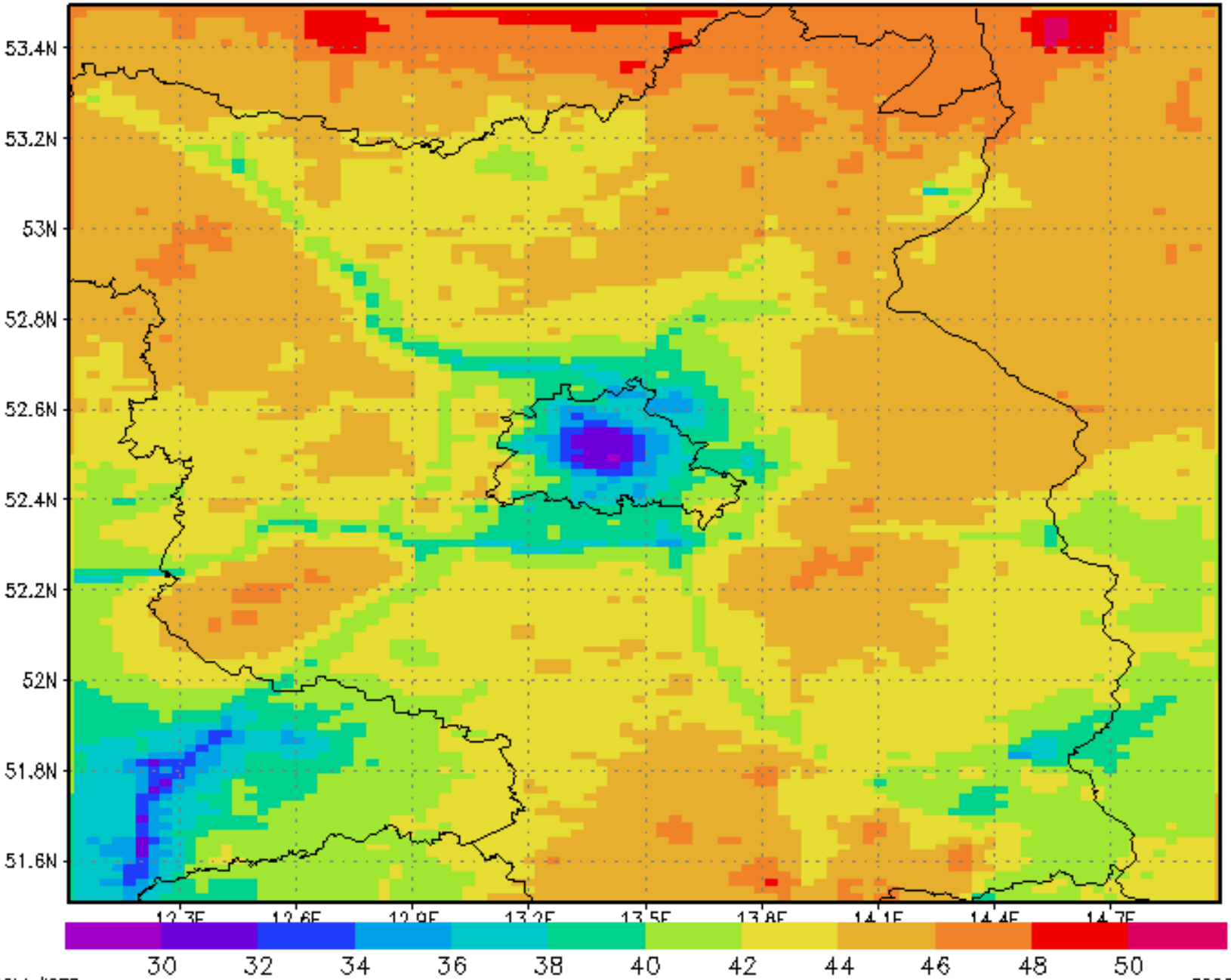


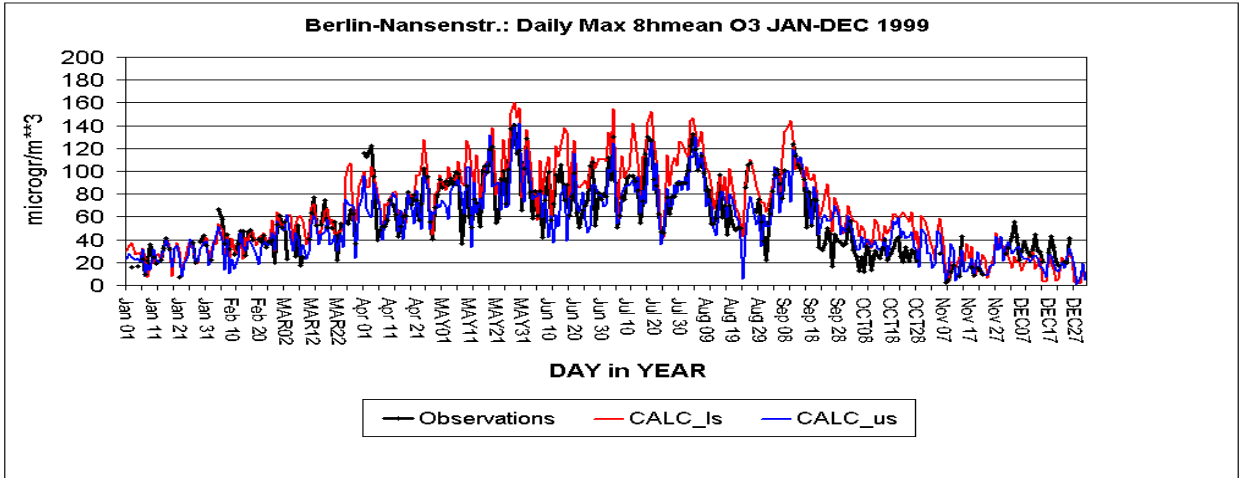


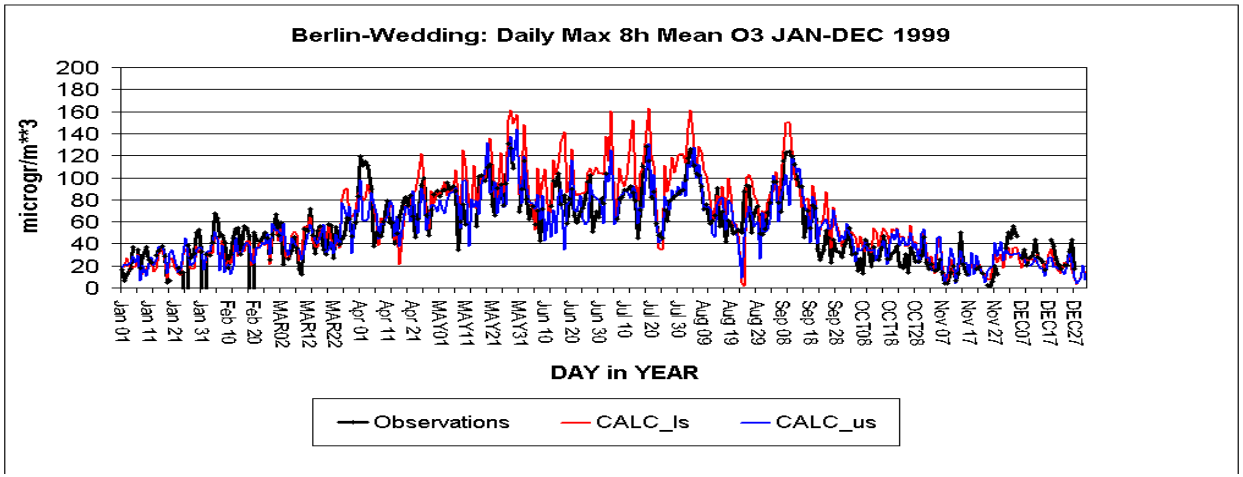


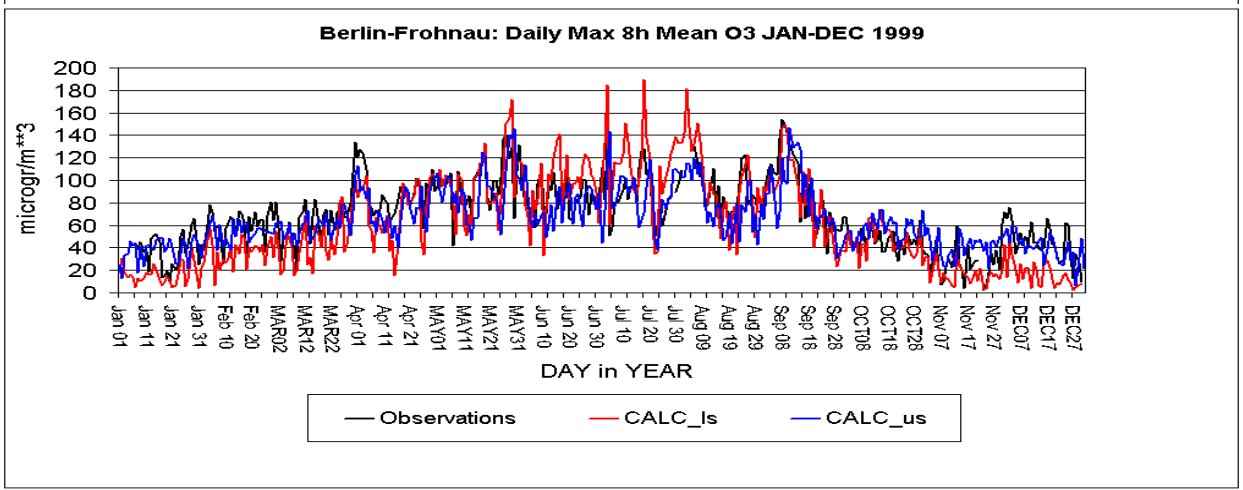


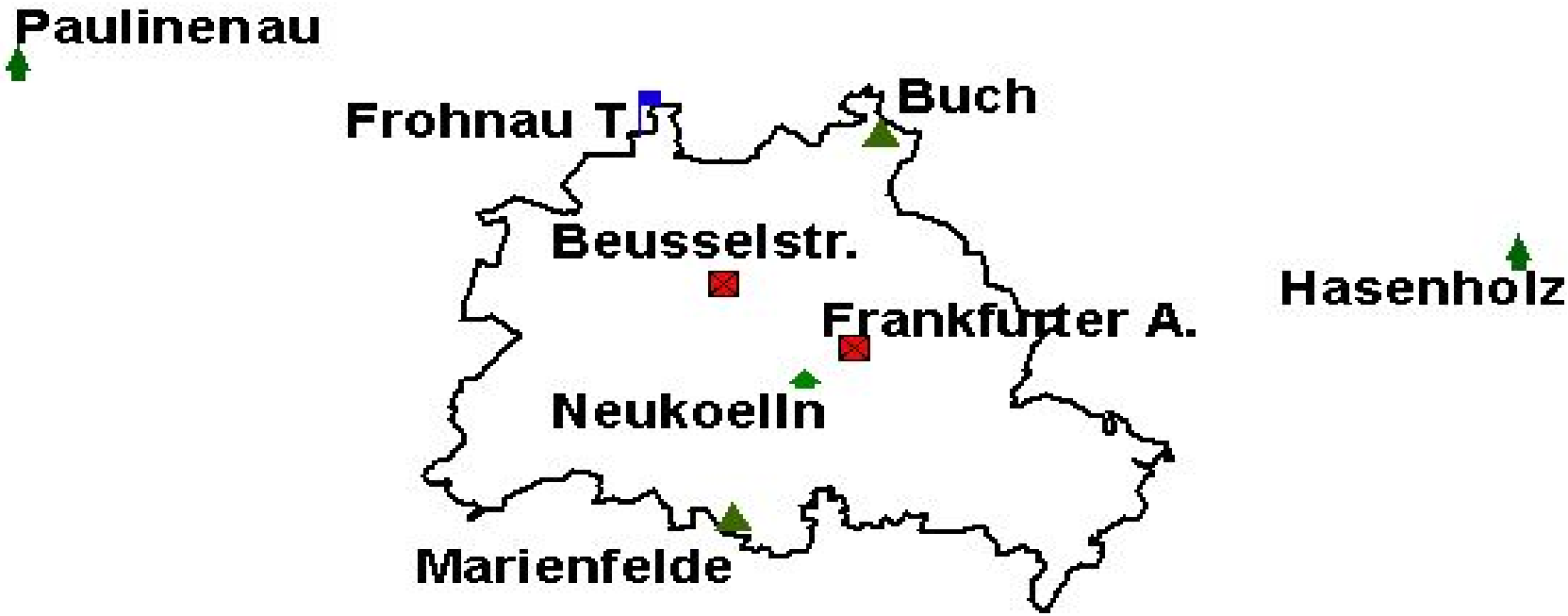
RCG: O3 ANNUAL MEAN in microgr/m3, 1999



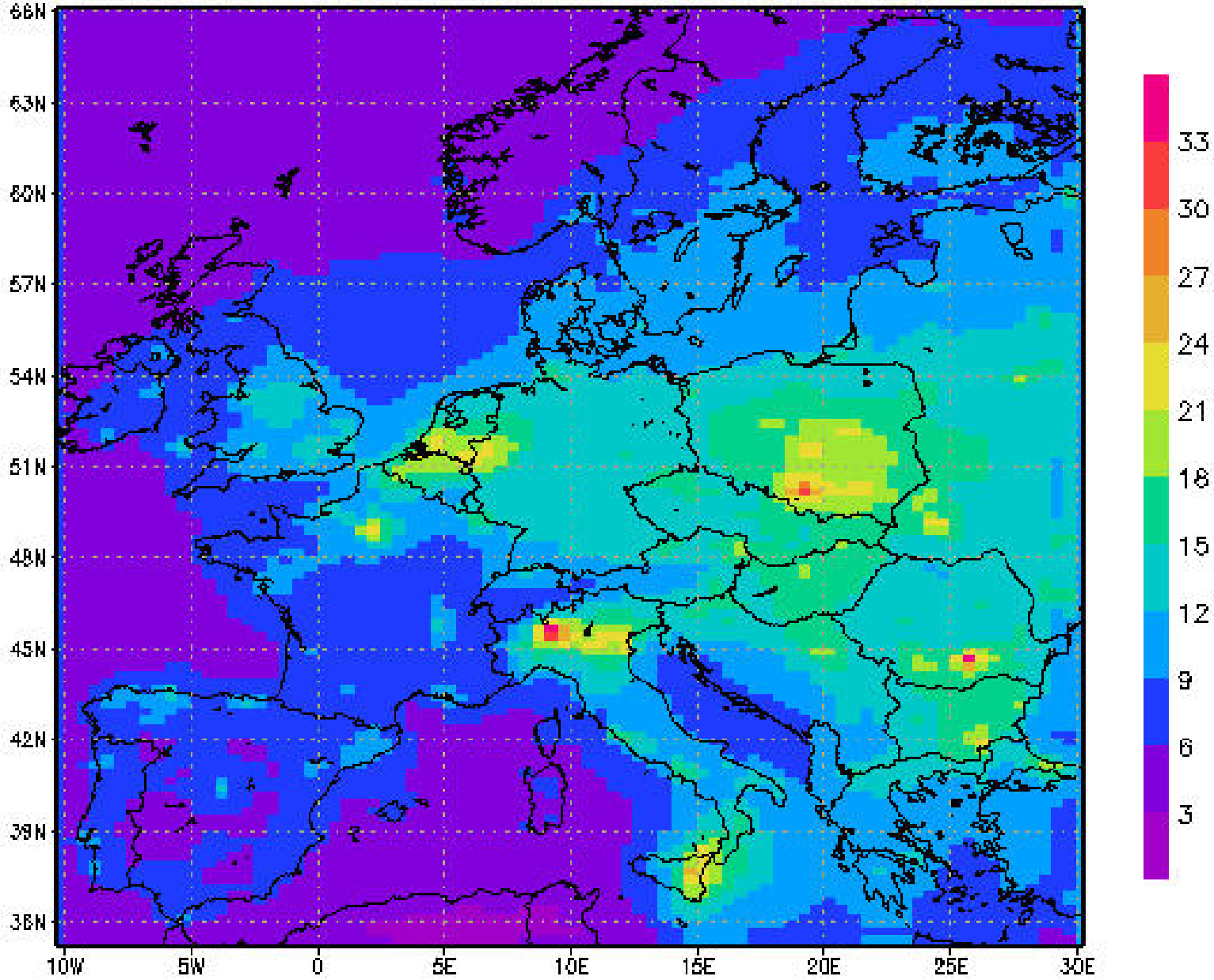

Berlin-Nansenstr.: Daily Max 8hmean O3 JAN-DEC 1999
microgr/m**3
DAY in YEAR
Observations
CALC_ls
CALC_us


Berlin-Wedding: Daily Max 8h Mean O3 JAN-DEC 1999
microgr/m**3
DAY in YEAR
Observations
CALC_ls
CALC_us


Berlin-Frohnau: Daily Max 8h Mean O3 JAN-DEC 1999
microgr/m**3
DAY in YEAR
Observations
CALC_ls
CALC_us


Paulinenau
Frohnau T.
Buch
Beusselstr.
Hasenholz
Frankfurter A.
Neukoelln
Marienfelde

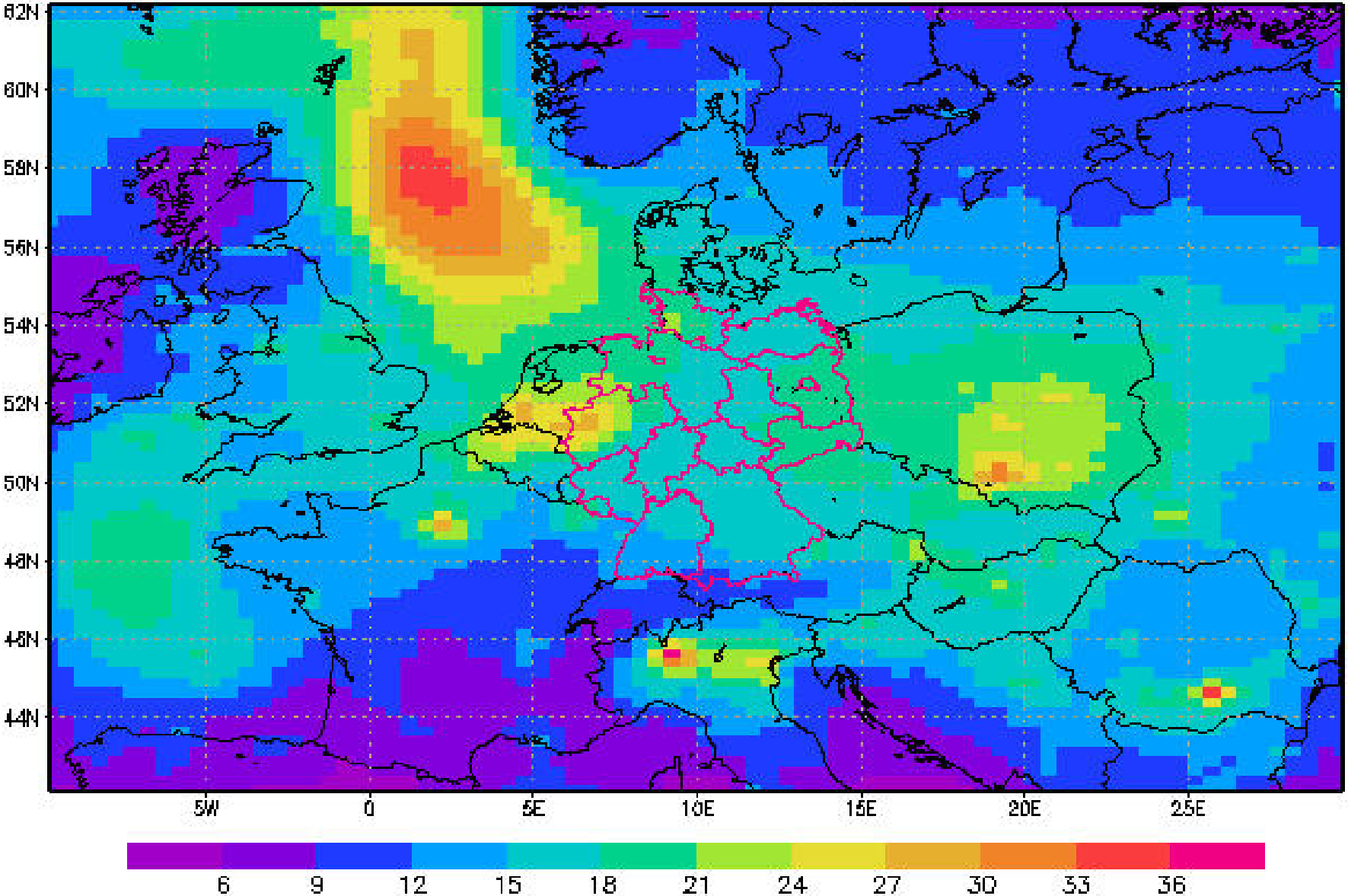
RCG: P10 Annual Mean MET 2001, E2000, microgr/m3



GrADS: COLA/IGES

2004-10-28-12:29

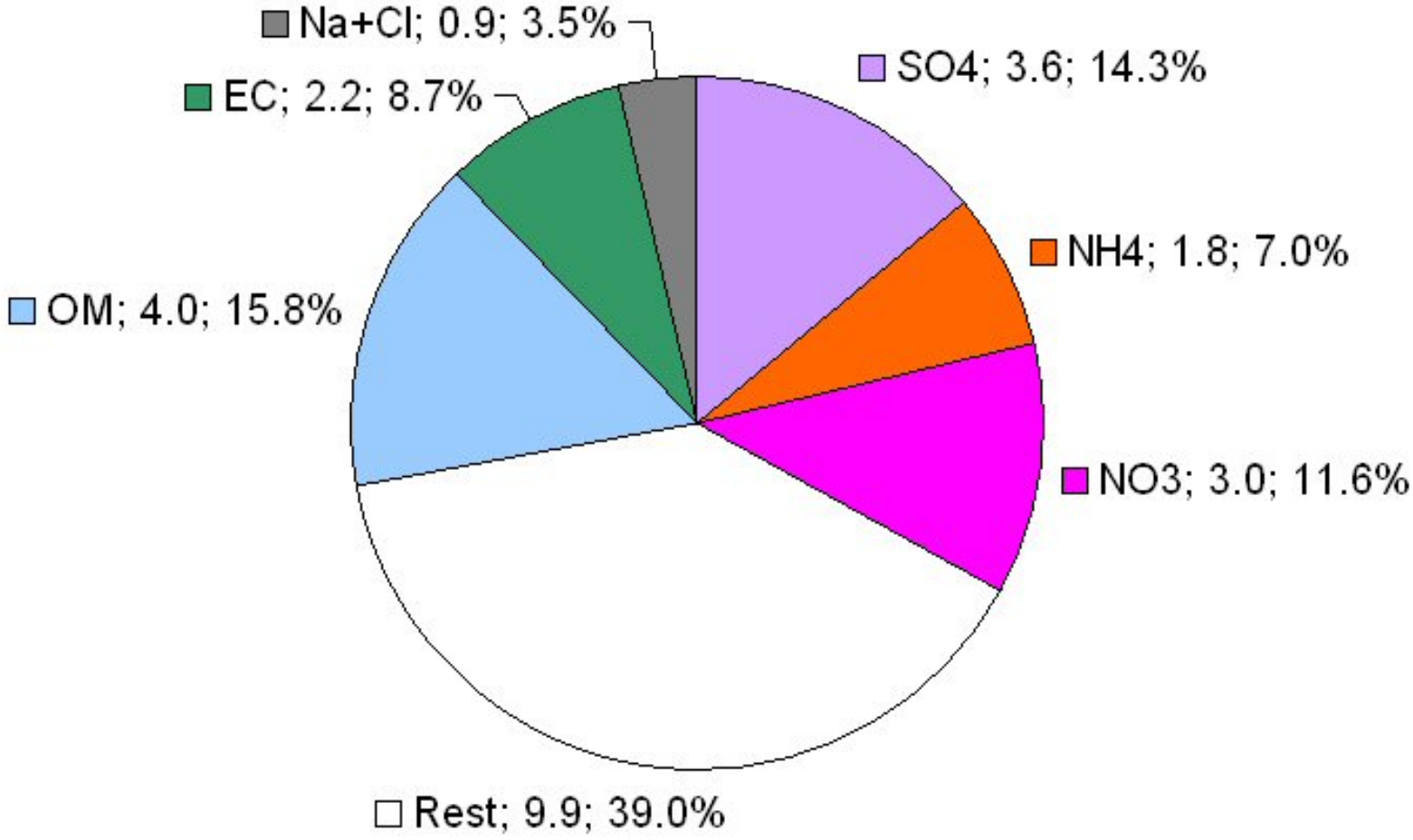
RCG: PM10 Annual Mean 2002 in microgr/m3 incl. sea salt aerosols



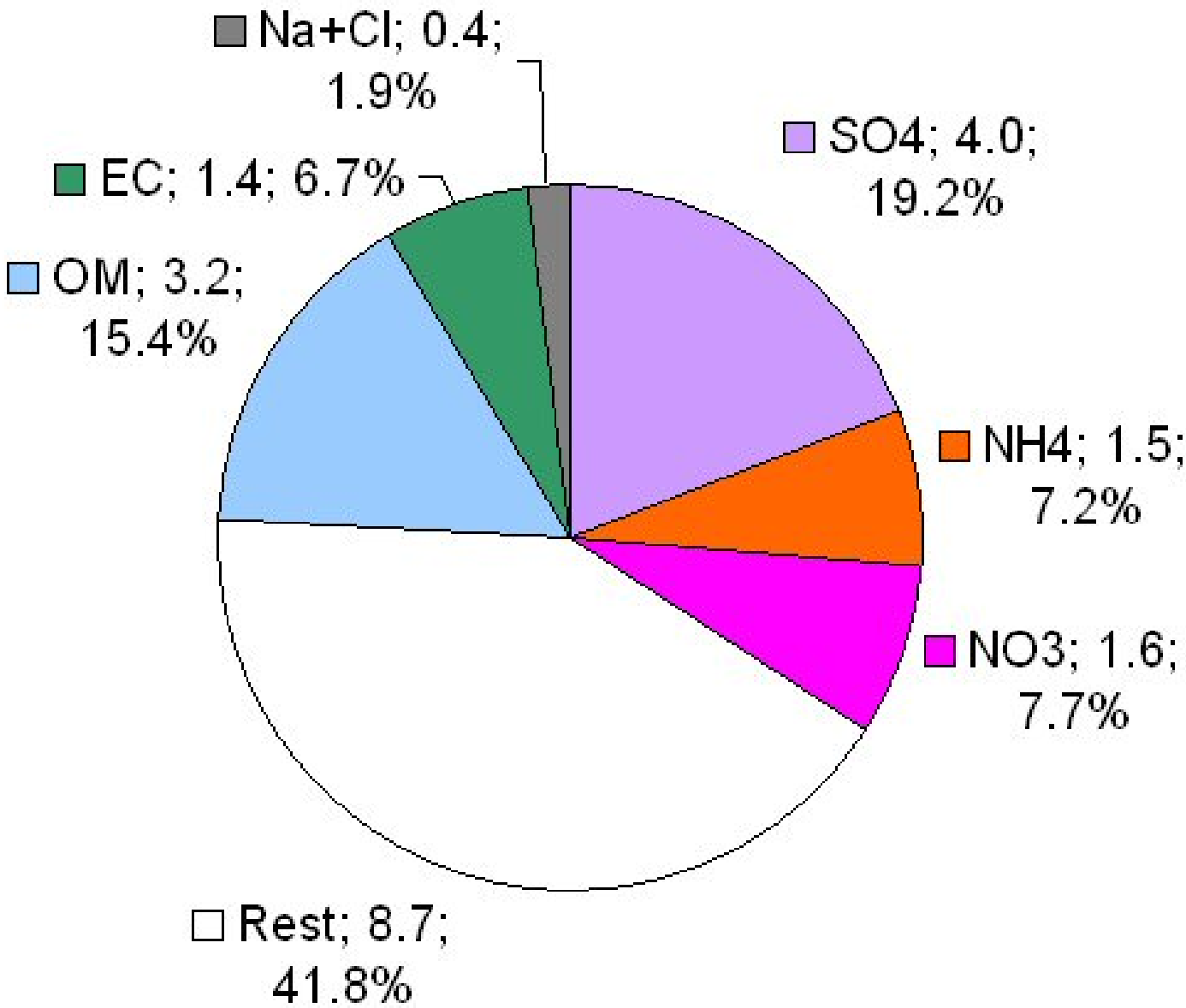
GrADS: COLA/IGES

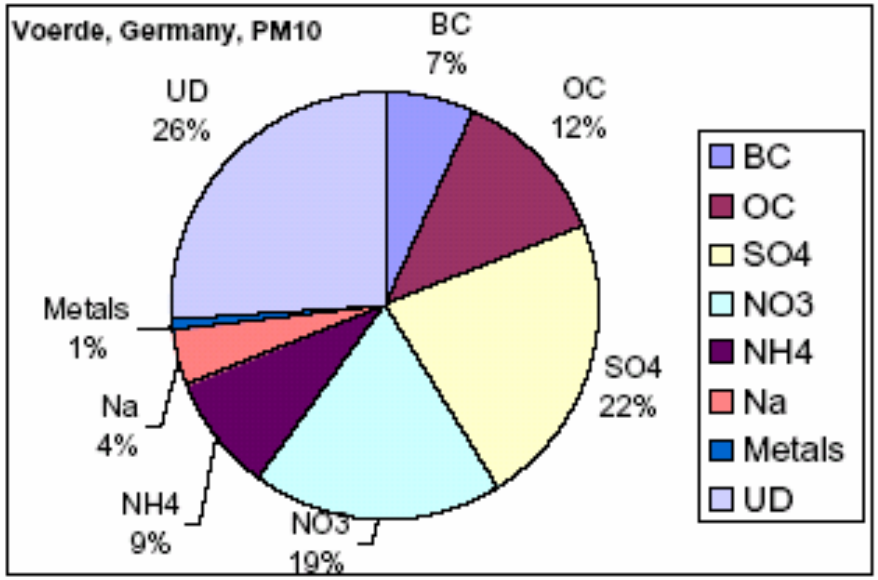
2004-06-24-14:46

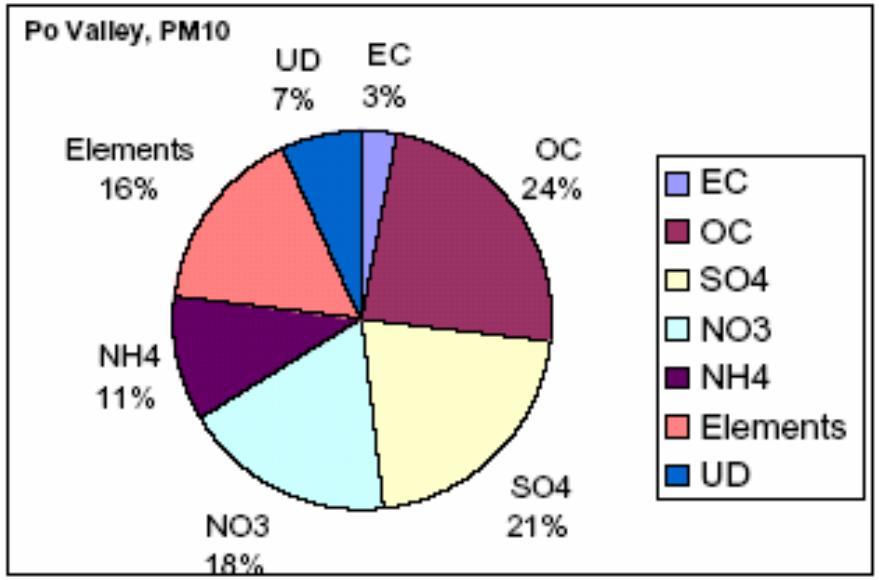
HOVERT (15.9.2001-15.9.2002): BERLIN-NANSENSTRASSE: PM10 COMPOSITION 2002, µgr/m3, and % of total PM10

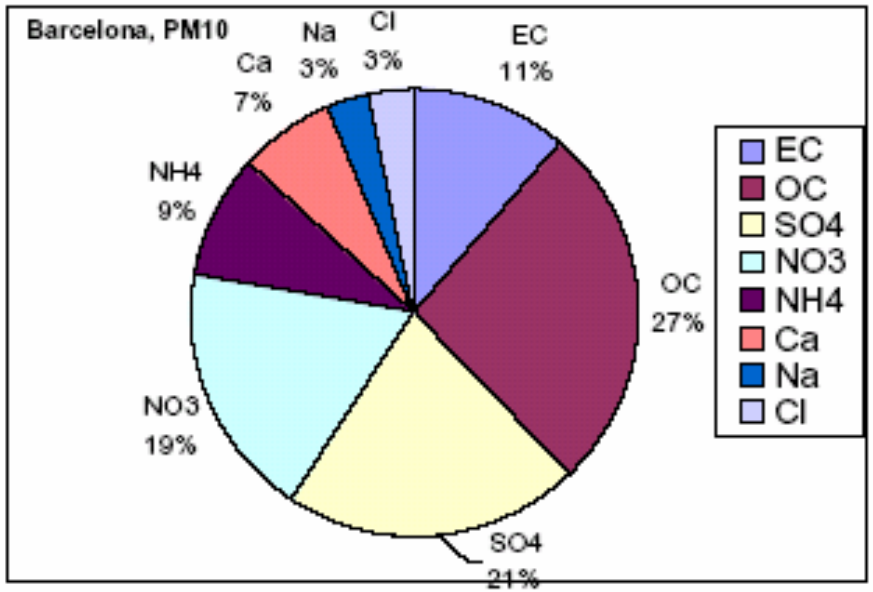


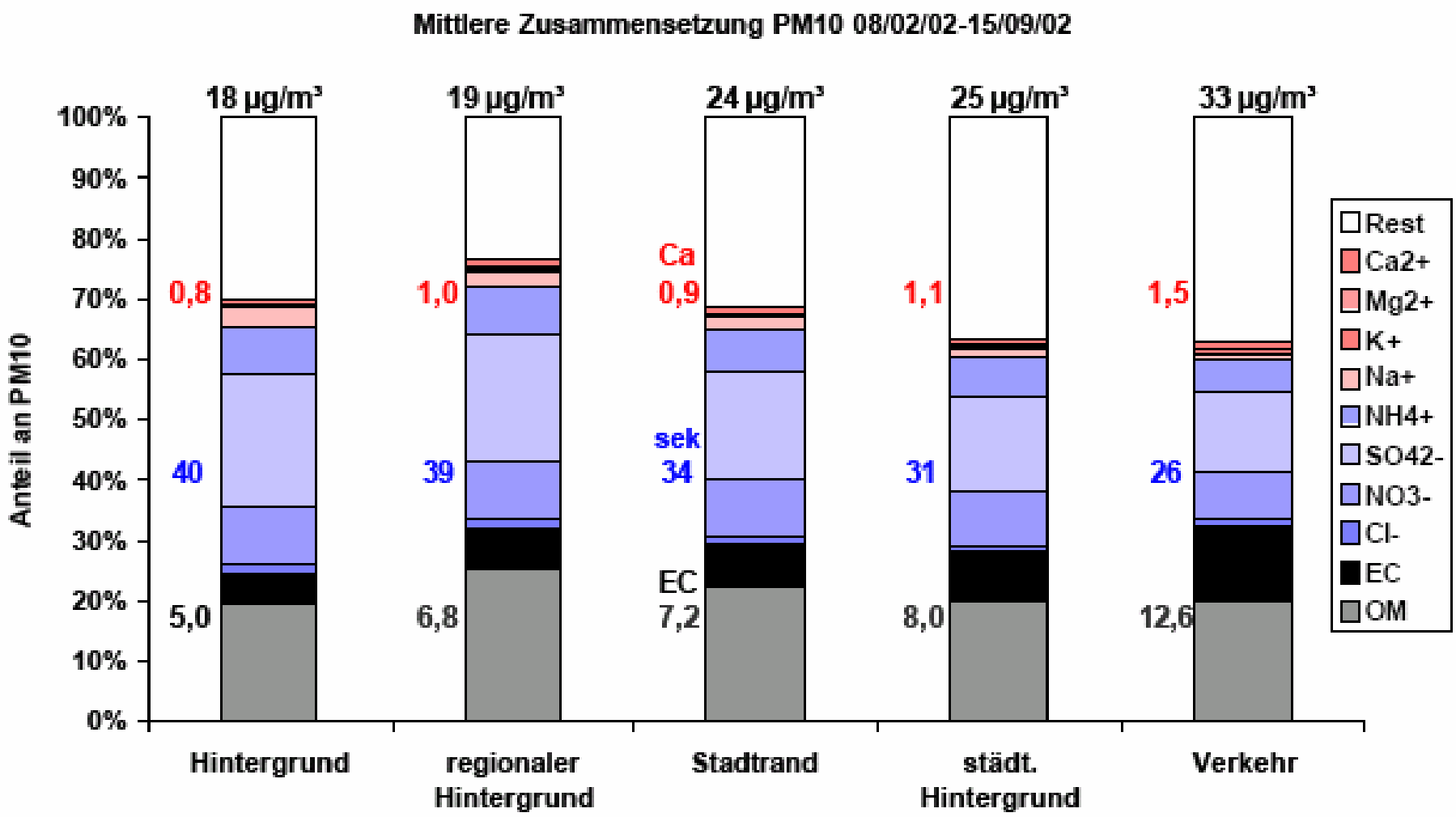
HOVERT (15.9.2001-15.9.2002): Hasenholz: PM10 COMPOSITION 2002, µgr/m3, and % of total PM10



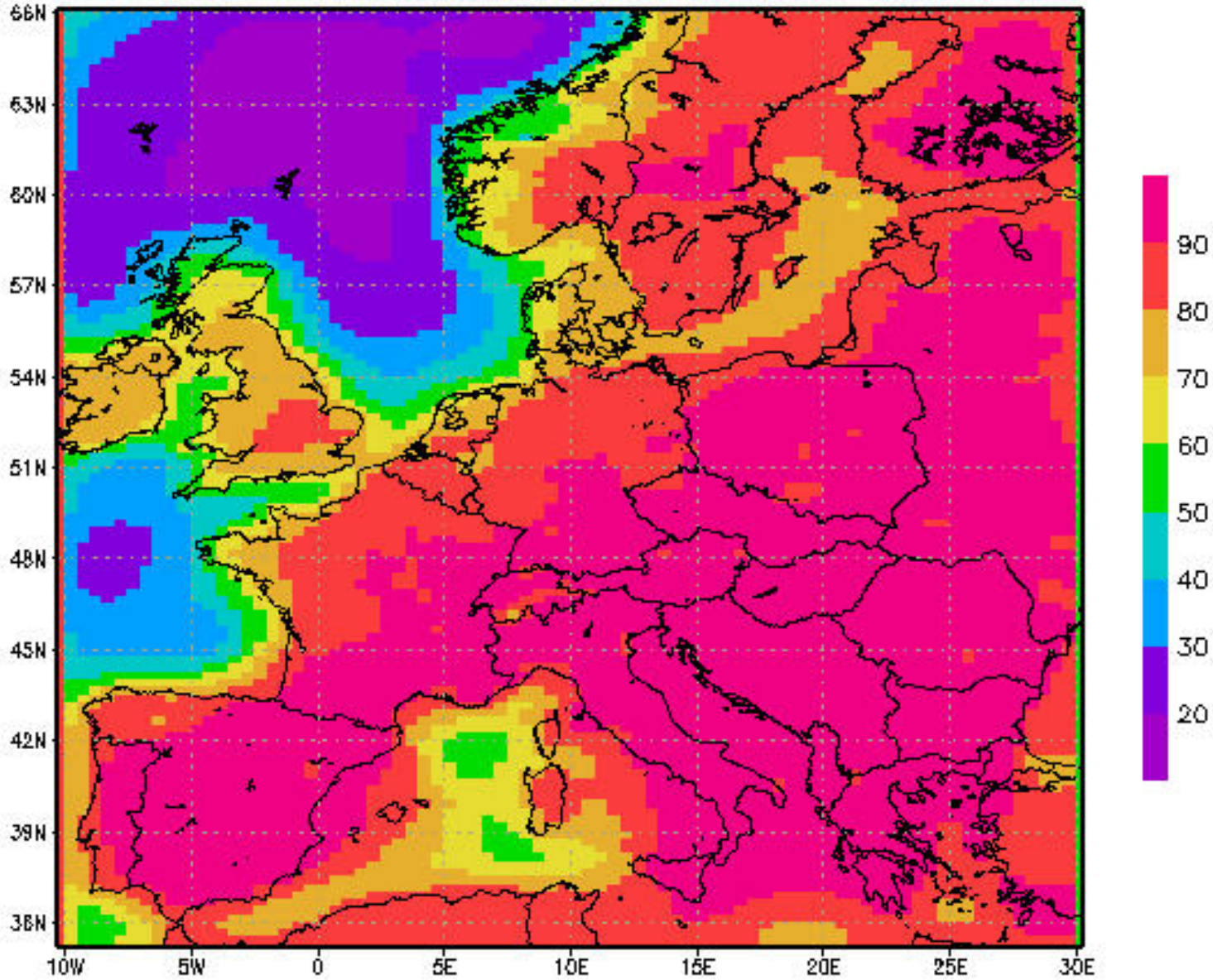

Voerde, Germany, PM10
BC
7%
OC
12%
SO4
22%
NO3
19%
NH4
9%
Na
4%
Metals
1%
UD
26%
BC
OC
SO4
NO3
NH4
Na
Metals
UD


Po Valley, PM10
EC
3%
OC
24%
SO4
21%
NO3
18%
NH4
11%
Elements
16%
UD
7%
EC
OC
SO4
NO3
NH4
Elements
UD


Barcelona, PM10
EC
11%
OC
27%
SO4
21%
NO3
19%
NH4
9%
Ca
7%
Na
3%
Cl
3%
EC
OC
SO4
NO3
NH4
Ca
Na
Cl

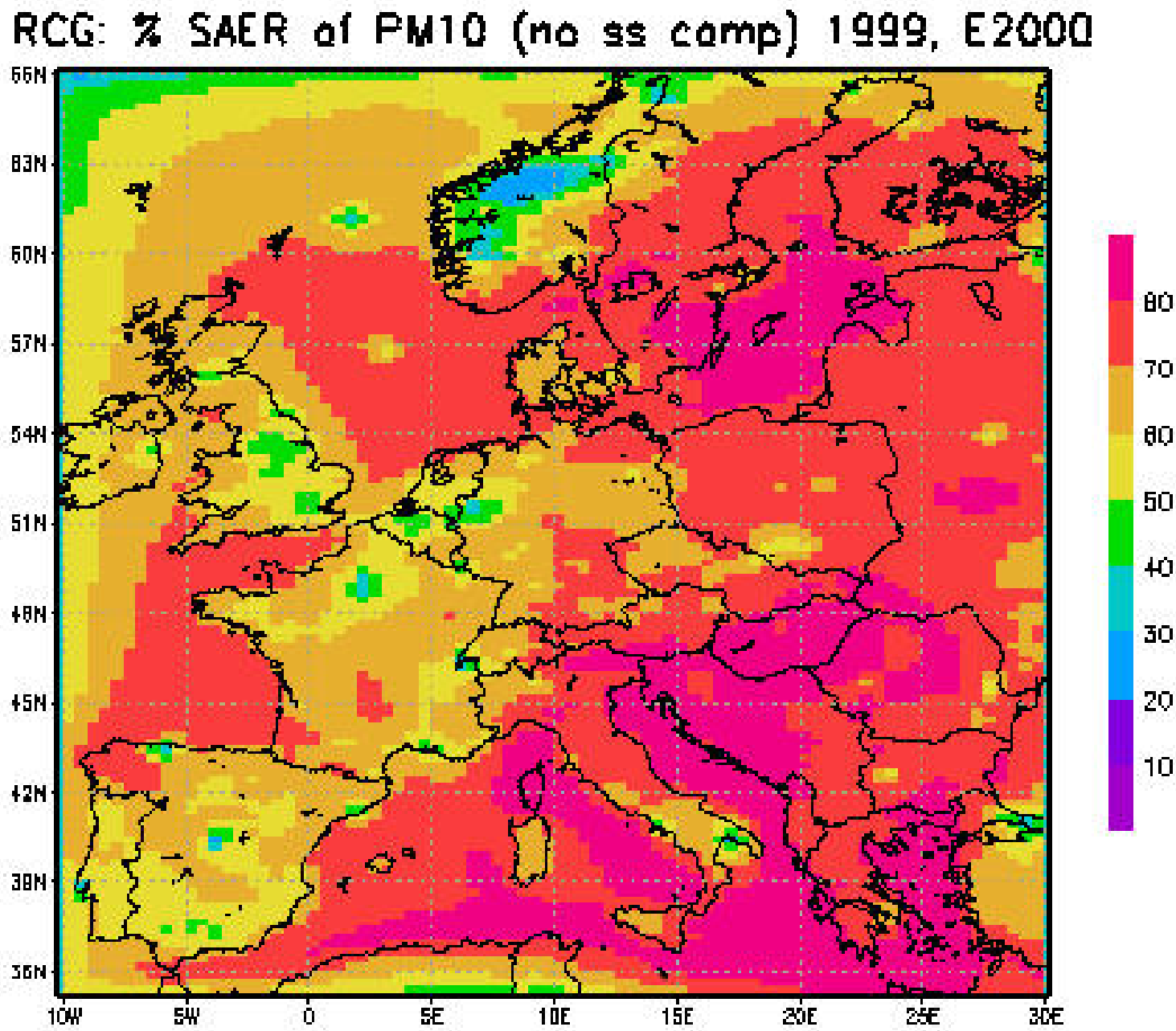

Mittlere Zusammensetzung PM10 08/02/02-15/09/02
18 µg/m³
19 µg/m³
24 µg/m³
25 µg/m³
33 µg/m³
Anteil an PM10
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0,8
40
5,0
1,0
39
6,8
Ca
0,9
sek
34
EC
7,2
1,1
31
8,0
1,5
26
12,6
Hintergrund
regionaler Hintergrund
Stadtrand
städt. Hintergrund
Verkehr
Rest
Ca2+
Mg2+
K+
Na+
NH4+
SO42-
NO3-
Cl-
EC
OM

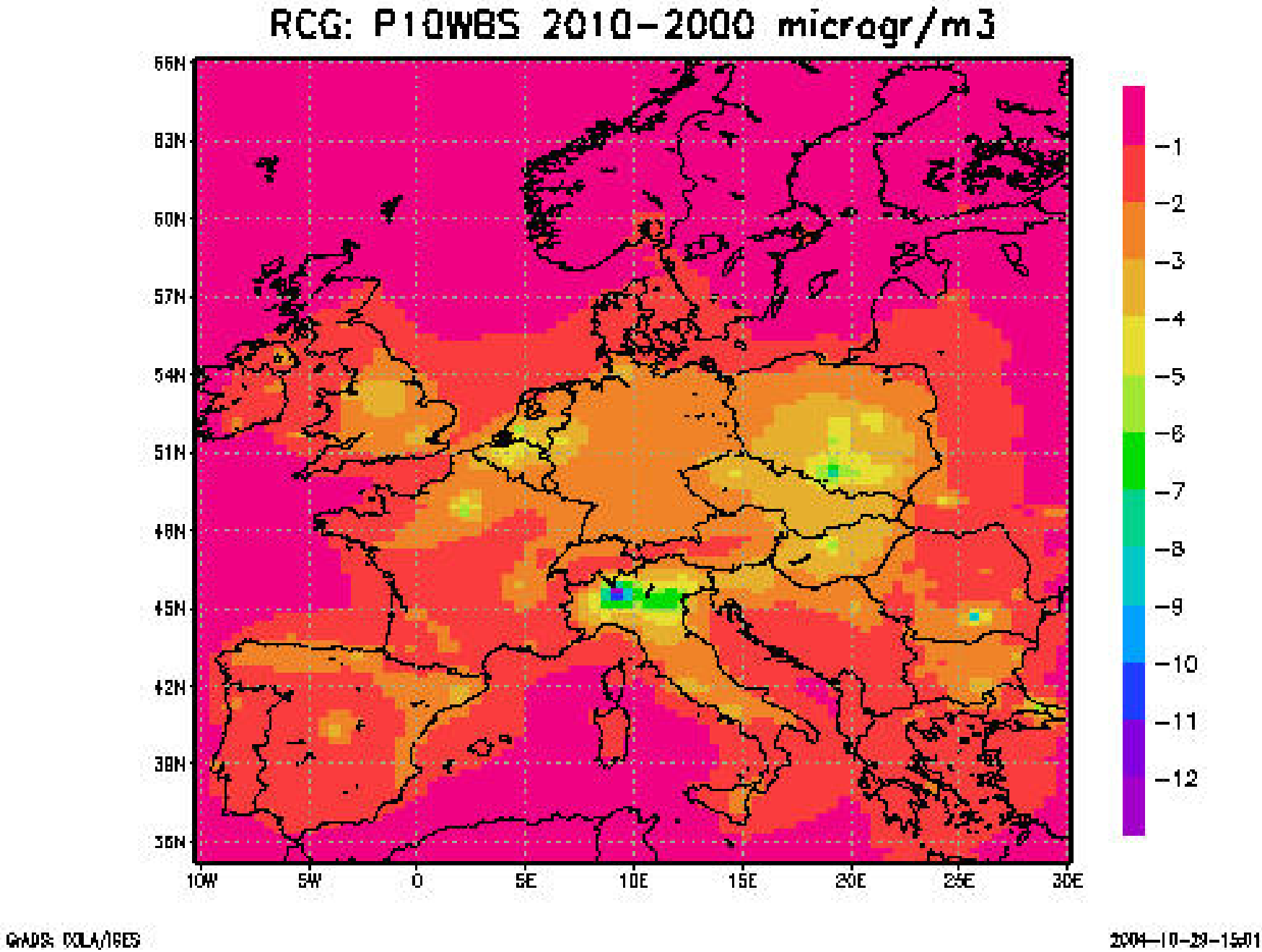
RCG: Percentage of PM10 that is PM2.5 Annual Mean 2000



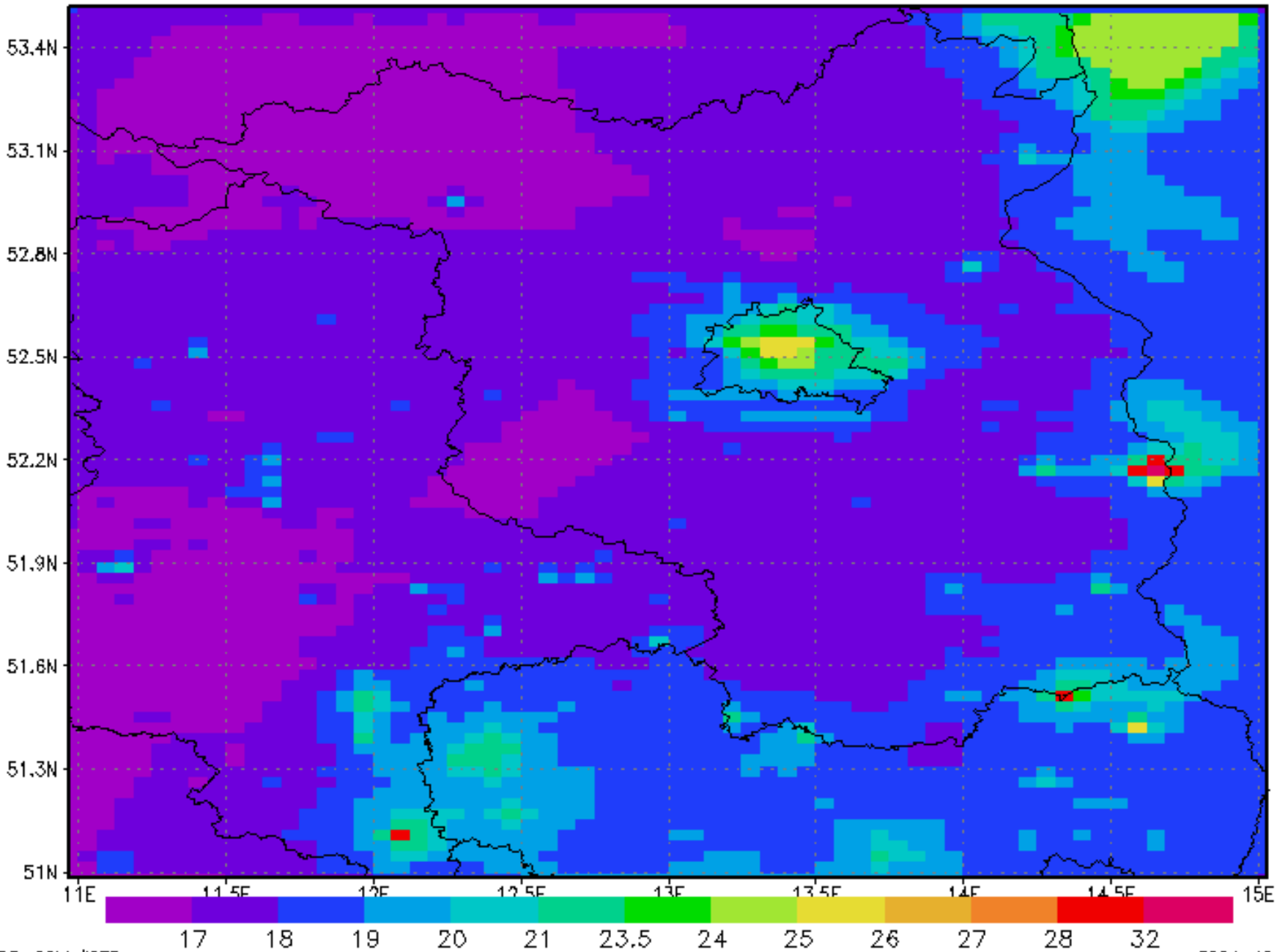
GrADS: COLA/IGES

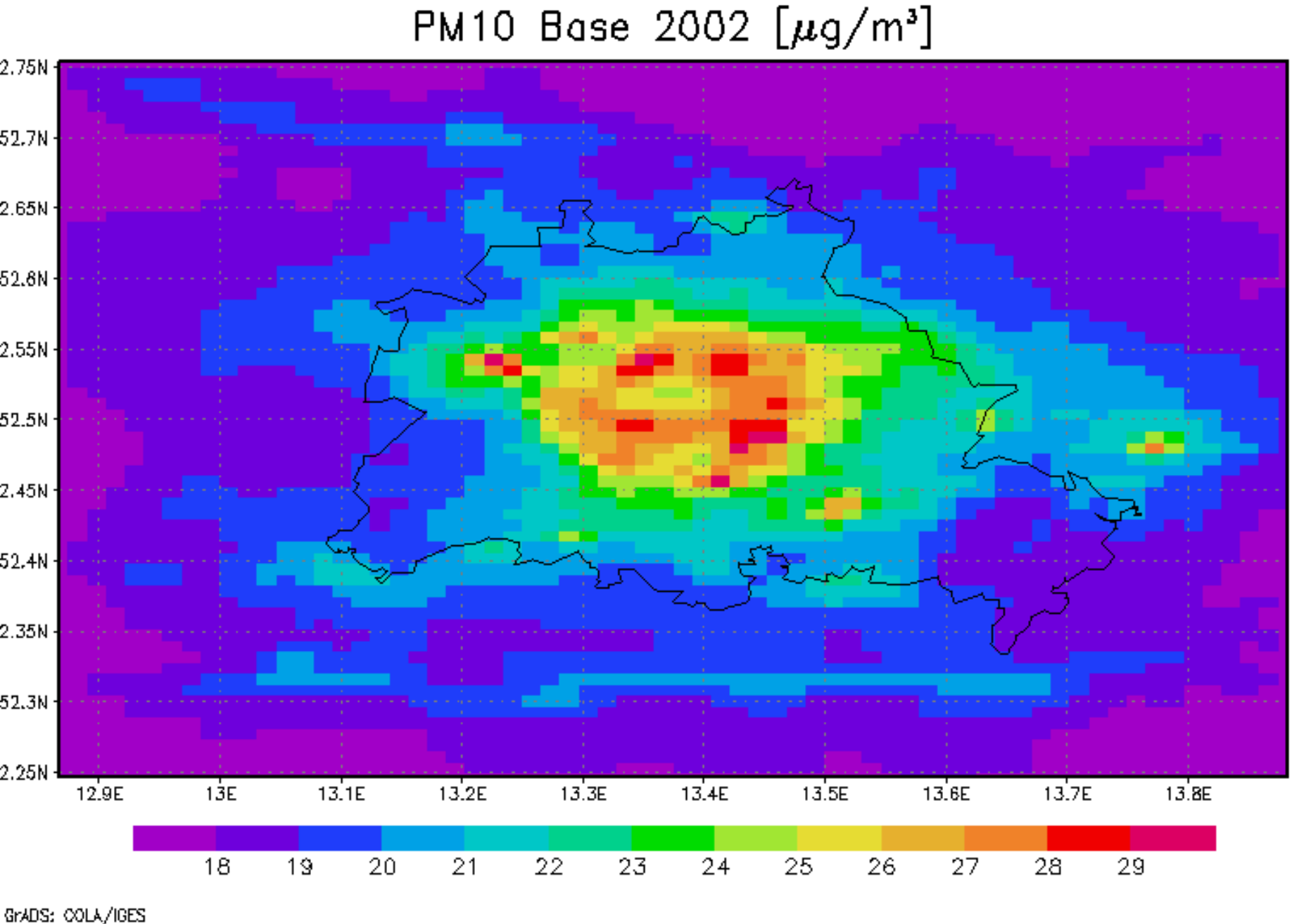
2004-10-18-14:44


RCG: % SAER of PM10 (no ss comp) 1999, E2000
66N
63N
60N
57N
54N
51N
48N
45N
42N
39N
36N
10W
5W
0
5E
10E
15E
20E
25E
30E
80
70
60
50
40
30
20
10
GrADS: COLA/IGES
2004-03-24-12:57

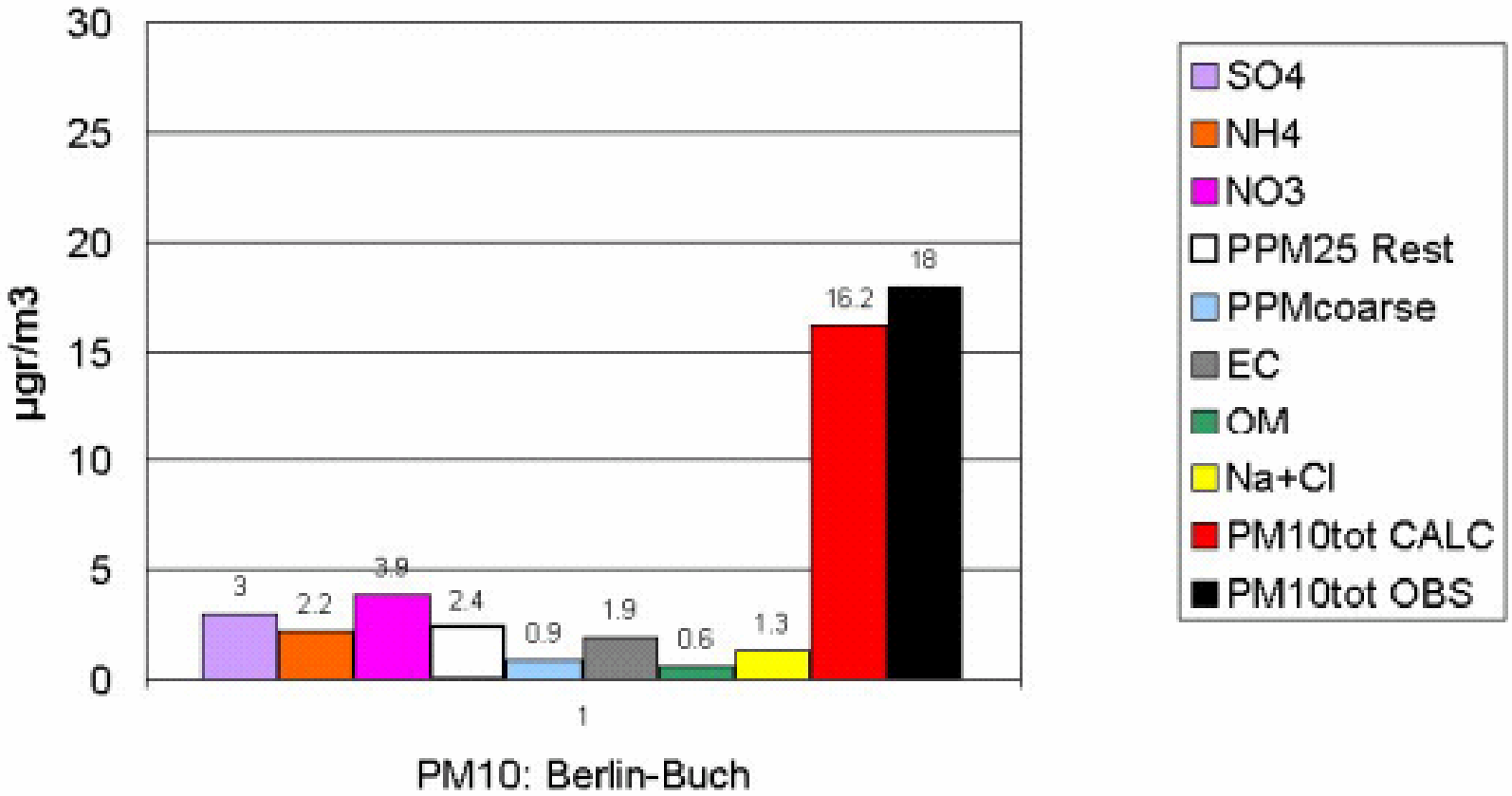

RCG: P10WBS 2010-2000 micragr/m3
66N
63N
60N
57N
54N
51N
48N
45N
42N
39N
36N
10W
5W
0
5E
10E
15E
20E
25E
30E
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
GrADS: COLA/IGES
2004-10-29-15:01

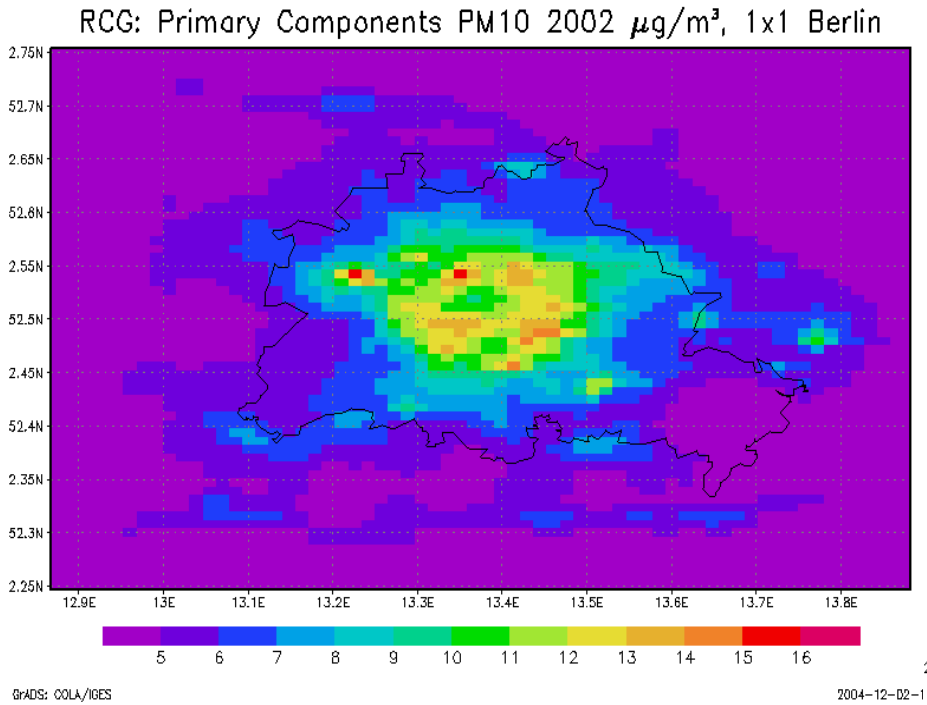
RCG: PM10 Annual Mean 2002 $\mu g/m^3$, 4x4 Berlin

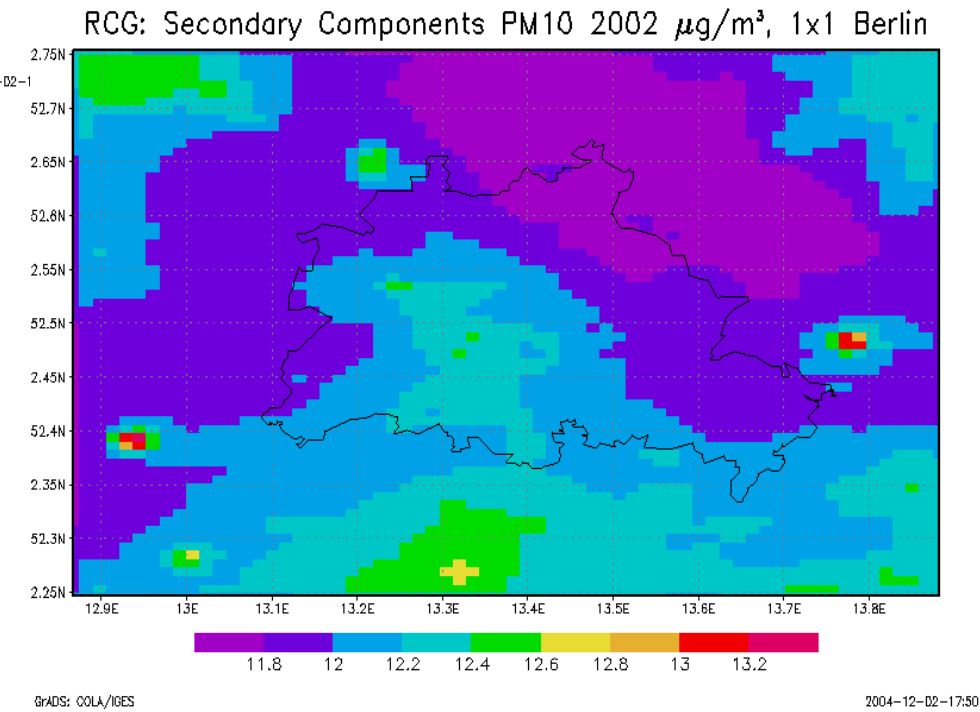


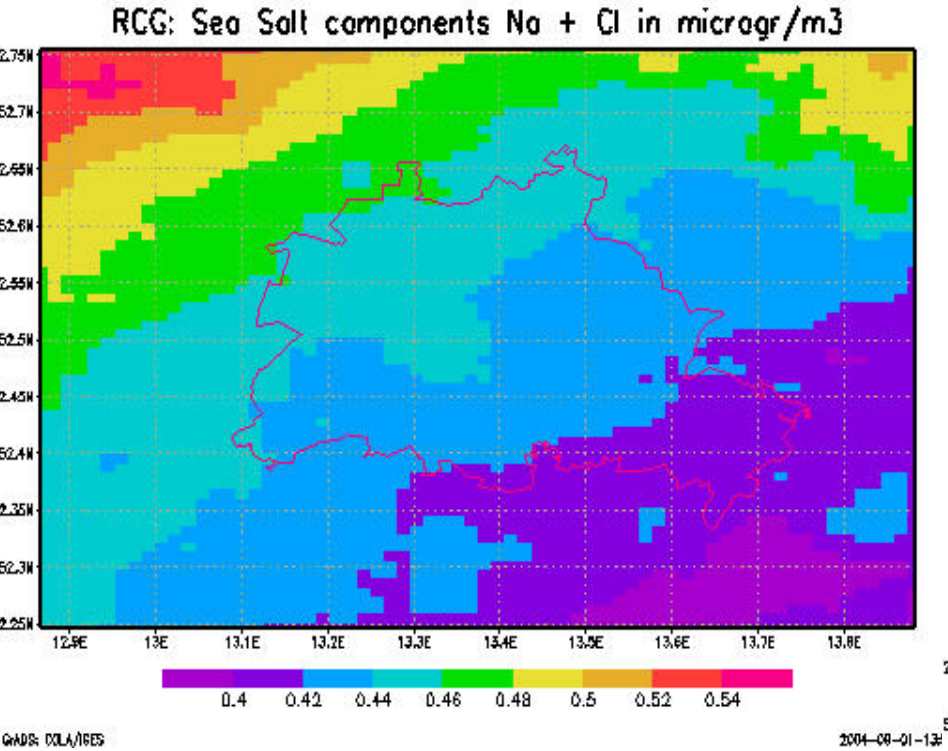

PM10 Base 2002 [µg/m³]
2.75N
52.7N
2.65N
52.6N
2.55N
52.5N
2.45N
52.4N
2.35N
52.3N
2.25N
12.9E
13E
13.1E
13.2E
13.3E
13.4E
13.5E
13.6E
13.7E
13.8E
18
19
20
21
22
23
24
25
26
27
28
29
GrADS: COLA/IGES

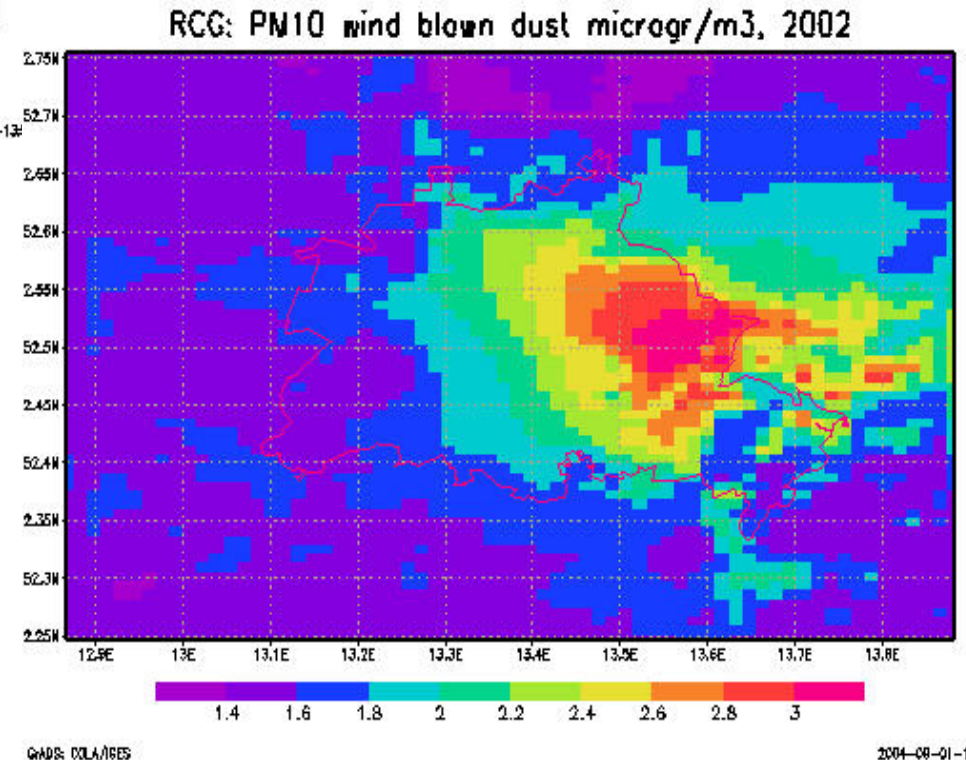
RCG: Zartau: PM10 COMPOSITION 1999




RCG: Primary Components PM10 2002 µg/m³, 1x1 Berlin
2.75N
52.7N
2.65N
52.6N
2.55N
52.5N
2.45N
52.4N
2.35N
52.3N
2.25N
12.9E
13E
13.1E
13.2E
13.3E
13.4E
13.5E
13.6E
13.7E
13.8E
5
6
7
8
9
10
11
12
13
14
15
16
GrADS: COLA/IGES
2004-12-02-1


RCG: Secondary Components PM10 2002 µg/m³, 1x1 Berlin
2.75N
52.7N
2.65N
52.6N
2.55N
52.5N
2.45N
52.4N
2.35N
52.3N
2.25N
12.9E
13E
13.1E
13.2E
13.3E
13.4E
13.5E
13.6E
13.7E
13.8E
11.8
12
12.2
12.4
12.6
12.8
13
13.2
GrADS: COLA/IGES
2004-12-02-17:50


RCG: Sea Salt components Na + Cl in microgr/m3
52.75N
52.7N
52.65N
52.6N
52.55N
52.5N
52.45N
52.4N
52.35N
52.3N
52.25N
12.9E
13E
13.1E
13.2E
13.3E
13.4E
13.5E
13.6E
13.7E
13.8E
0.4
0.42
0.44
0.46
0.48
0.5
0.52
0.54
GrADS: COLA/IGES


RCG: PM10 wind blown dust microgr/m3, 2002
52.75N
52.7N
52.65N
52.6N
52.55N
52.5N
52.45N
52.4N
52.35N
52.3N
52.25N
12.9E
13E
13.1E
13.2E
13.3E
13.4E
13.5E
13.6E
13.7E
13.8E
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3
GrADS: COLA/IGES