AirBase: a valuable tool in air quality assessments at a European and local level

ETC/ACM Technical Paper 2012/4
April 2012

Frank de Leeuw

Author affiliation
Frank de Leeuw: National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands.

DISCLAIMER

This ETC/ACM Technical Paper has not been subjected to European Environment Agency (EEA) member country review. It does not represent the formal views of the EEA.

SUMMARY

The mutual exchange air quality data between the EU Member States started in 1975 with data on "certain pollutants and suspended particulates" (Decision 75/3441/EEC). In 1982 this decision was replaced by a decision which included SO_2, NO_x, CO, ozone, heavy metals and particulates (Decision 82/459/EEC). The third Exchange of Information (EoI) decision dates from January 1997 (97/1010/EC). This decision will remains in force until 1 January 2014 when it will be replaced by Commission Decision 2011/850/EU (Commission Implementing Decision laying down rules for the air quality directives 2004/107/EC and 2008/50/EC as regards the reciprocal exchange of information and reporting on ambient air quality).

In the 1990's electronic archiving of the air quality data started into two separate databases labelled as *APIS* and *GIRAFE*. In APIS the air quality data was stored while in GIRAFE the meta-information of networks and monitoring stations was handled. In 1995 the European Topic Centre on Air Quality, one of the predecessors of the current Topic Centre, supported the EEA in the review of both data bases and started the developed of an European air quality information system meeting the needs and requirements of the Member States, the Commission and other potential clients. This resulted in the system with the Data Exchange Module (DEM) as vehicle to transfer data from the EU Member States and from 11 other European countries to the EEA and AirBase as the European air quality database.

To demonstrate the use of AirBase in various types of air quality assessments, we present in the first chapters shortly the European air quality as observed in 2010. A more extensive analysis will be provided in a report *Air Quality in Europe - 2012* to be published by EEA later this year. In the remaining chapters we present various assessments of air quality related phenomena. These phenomena are not discussed *in extenso*; main purpose of this chapter is to show the use of AirBase data in some less obvious topics. Further a discussion on the precursors of ozone is given in Chapter 5. In Chapter 6 the consequences of missing data are discussed.

CONTENTS

1. INTRODUCTION

AirBase is a publicly available database containing European-wide information on air quality monitoring networks, stations and observational data. The European Environmental Agency (EEA) has been assisted by the European Topic Centre on Air Pollution and Climate Change Mitigation (ETC/ACM) with development and operation of AirBase.

Air quality data from 38 European countries, including all 32 EEA member countries, is collected under the Council Decision 97/101/EC (known as the *Exchange of Information* decision). In the latest version (Mol and van Hooydonk, 2012) meta-information on nearly 8000 stations and concentration data of more than 40 pollutants are available. Data over 2010 has been delivered for about 4600 stations. The oldest data in AirBase is from 1973; however, a reasonable to good spatial coverage over Europe is available since 1997-2000.

AirBase has been used in a large number of air quality studies: a simple search[1] on the keyword "airbase" indicated that AirBase information has been used in 74 papers published in *Atmospheric Environment* alone since 2000. AirBase information has been used for numerous assessments both for the European Commission as well as for the EEA (examples may be found at the web site of the ETC/ACM[2]).

In this report we present shortly the European air quality as observed in 2010. A more extensive analysis will be provided in a report *Air Quality in Europe - 2012* to be published by EEA later this year. In the remaining chapters we present various assessments of air quality related phenomena. These phenomena are not discussed *in extenso*; main purpose is to demonstrate the use of AirBase in describing some less obvious topics. Further a discussion on the precursors of ozone is given in Chapter 5. In Chapter 6 the consequences of missing data are discussed.

The statistical data presented here has been extracted from the AirBase (meta)data files by means of an Excel macro. This macro extracts and selects statistical data, aggregated exceedance information and relevant meta information (see Annex B in Mol and van Hooydonk (2012) for a description of the available statistical data) for a pollutant, period and countries defined by the user. The macro is available at the ETC/ACM web site[3]; the AirBase metadata is in the form of XML-files available from the EEA data service[4].

---

[1] accessed 29 March 2012.

[2] see http://acm.eionet.europa.eu/reports

[3] See http://acm.eionet.europa.eu/databases/airbase/airbasexml/index_html for the macro and additional documentation.

[4] See http://www.eea.europa.eu/data-and-maps/data/airbase-the-european-air-quality-database-3 ; the most convenient is to download the *all country XML-file.*

2. STATE OF THE AIR QUALITY FOR SELECTED POLLUTANTS

In addition to the more technical aspects of the 2010-data submission process presented in Mol and van Hooydonk, this section will present a preliminary evaluation[5] of the 2010 air quality data. More extensive discussions on the state of the European ambient air has and will be provided in the air pollution and related reports prepared by EEA and ETC/ACM (e.g. by means of the core set of indicators or in the forthcoming report on European Air Quality (EEA, 2012 in preparation).

The chapter will briefly describe the current (2010) air quality status and the long-term changes in concentrations are also discussed. Focus will be on the pollutants listed in the Air Quality Directive (EU, 2008), that is, SO_2, NO_2, PM_{10} and $PM_{2.5}$, CO, C_6H_6 and O_3. Lead and the other pollutants (arsenic, cadmium, nickel and benzo(a)pyrene) listed in the 4th Daughter Directive (EU, 2004a) will only briefly be discussed. An analysis (Barrett *et al.* 2008) has shown that, with the exception of a few (industrial) hotspots, the heavy metal concentrations are well below the limit (LV) or target value (TV), however, benzo(a)pyrene (B(a)P) may form a potential risks for human health in various parts of Europe.

The concentrations measured in 2010 will be compared with two sets of reference values. One set corresponds to the WHO air quality guidelines (AQG; WHO 1987, 2000, 2006); the second set corresponds to the limit and target values as set in the EU Directives.

For pollutants which are carcinogenic to humans, there is no safe level of exposure. The WHO does not recommend guideline values for these pollutants. Environmental regulations for carcinogens commonly aim to limit the individual risk of premature death to ~10^{-6} - 10^{-5} for pollutants in ambient air. Based on the unit risk estimates given by the WHO (1987, 2000, 2006) a reference level associated with an excess cancer risk of 1 in a population of 100 000 has been calculated. The two sets of reference levels are summarised in Table 1.

The air quality in 2010 is described here in a number of maps showing annual mean concentrations together with availability and geographical distribution of the reporting stations. The air quality in relation to the reference values is presented in frequency distribution graphs. In these graphs for each station type the (relative) frequency distribution of concentrations measured at each station type is shown. The station types are: *rural* (=rural background), *urban* (= (sub)urban background), *traffic* (any type of area) and *other* (any type of area; this subset includes mainly industrial; stations and a limited number of stations with an ill-defined classification). In each graph the bin size equals 10% of the reference value, for example in the frequency distribution graph of the PM_{10} annual mean value (having a limit value of 40 µg/m^3), the concentration bins runs from 0 - 4; 4 - 8; 8 - 12; 12 - 16 µg/m^3;…etc. Additionally, we present for some pollutants the EU limit or target values a simplified frequency distribution at the national level. These graphs show the minimum, maximum, mean, 25- and 75-percentile values (the latter two only in case there are four or more stations available) calculated for all operational stations in each of the 27 MS. These graphs give a possibility to compare the air quality between the Member States; however, care should be taken as part of the differences might be caused by differences in network design (e.g. relative differences in the number of hot-spot (traffic, industrial) stations).

In case the EU limit value is expressed as a maximum allowable number of exceedances (N_{exc}) of a specified threshold value, the corresponding percentile value has been evaluated. This is in contrast with the assessment presented in the 2009-report (Mol et al, 2011) where the (N_{exc}+1)[th] highest value has been evaluated. There is compliance with the limit value if the (N_{exc}+1)[th] highest value or the corresponding percentile value is below the threshold level. The additional error introduced when data is partly missing (that is, for data coverages of less than 100%), is lower when the percentile value is used in stead of the N_{exc}+1)[th] highest value, see Chapter 6 for further discussion.

---

[5] In this assessment data from AirBase-v6, (published on 8 February 2012; http://www.eea.europa.eu/data-and-maps/data/airbase-the-european-air-quality-database-6) has been used.

In the maps, and in the trend graphs only stations having a data coverage of more than 75% have been included; for benzene the data coverage criterion has been set to 50% (Working Group on benzene, 1998) while for the heavy metals and B(a)P a coverage criterion of 14% is used (Mol *et al*, 2010). By accepting data coverage of less than 100% it is implicitly assume that the missing data are randomly distributed over the year. If this would not be the case a systematic error might be introduced. In Chapter 6 some thoughts about this concept of "randomness" are presented. The selection criteria discussed in that chapter have not been implemented here.

The frequency distribution graphs related to the WHO reference levels are presented for all reporting countries; the graphs related to the EU limit or target values are presented for the EU27 Member States only. Note that in this report the data shown in maps and in the frequency distribution graphs relates to the year 2010, also in the cases when the EU limit or target value is defined as a three- or five-year averaged values (i.e. the ozone target values set for the protection of human health and ecosystems and the $PM_{2.5}$ Averaged Exposure Indicator, AEI).

Table 2.1. Reference values based on WHO guidelines and limit and target values defined by the EU for SO₂, NO₂, NOₓ, PM₁₀, PM₂.₅, lead, benzene, CO, O₃, arsenic, cadmium, nickel and benzo(a)pyrene to be met in 2010 unless indicated otherwise.

Pollutant	period	WHO	EU limit and target values (d)	No of allowed exceedances	percentile value	Target date
Threshold values set for the protection of human health						
SO_2	Hourly average		350 µg/m^3	24 hours/yr	99.73	
	Daily average	20 µg/m^3	125 µg/m^3	3 days/yr	99.18	
NO_2	Hourly average	200 µg/m^3	200 µg/m^3	18 hours/yr	99.79	
	Annual average	40 µg/m^3	40 µg/m^3			
PM_{10}	Daily average	50 µg/m^3	50 µg/m^3	35 days/yr	90.41	
	Annual average	20 µg/m^3	40 µg/m^3			
$PM_{2.5}$	Annual average	10 µg/m^3	25 µg/m^3			1 Jan 2015 [b]
	Averaged exposure indicator (AEI)		20 µg/m^3	based on 3 year average		2015
	Exposure reduction target		Percentage reduction (c)	based on 3 year average		2020
lead	Annual average	0.5 µg/m^3	0.5 µg/m^3			
CO	8h running average (a)	10mg/m^3	10mg/m^3			
benzene	Annual average	1.7 µg/m^3 (g)	5 µg/m^3			
ozone (h)	8h running average (a)	100 µg/m^3	120 µg/m^3 (TV)	25 days/yr	93.15	
arsenic	Annual average	6.6 ng/m^3 (g)	6 ng/m^3 (TV)			1 Jan 2013
cadmium	Annual average	5 ng/m^3	5 ng/m^3 (TV)			1 Jan 2013
nickel	Annual average	25 ng/m^3 (g)	20 ng/m^3 (TV)			1 Jan 2013
benzo(a) pyrene	Annual average	0.12 ng/m^3 (g)	1 ng/m^3 (TV)			1 Jan 2013
Threshold values set for the protection of vegetation or ecosystems						
SO_2	Annual average		20 µg/m^3			
	winter average		20 µg/m^3			
NOx	Annual mean		40 µg/m^3 (e)			
ozone (h)	AOT40 (f)	10 (mg/m^3).h	18 (mg/m^3).h (TV)			

(a) daily maximum of 8h running averaged concentrations;
(b) enters into force 1 Jan 2010 as target value;
(c) percentage reduction depending on the AEI value in 2010;
(d) limit value unless indicated otherwise;
(e) measured as NO2;
(f) the UNECE CLRTAP has set a critical level (averaging period April-September) for forest; the EU TV has bend set for an averaging period May-July;
(g) human carcinogen, no safe level for inhalation exposure can be recommended; the given value corresponds to an excess lifetime risk level of 10^{-5};
(h) in compliance checking an average over three (human health) or five (vegetation) years should be used.

3. 2010 Air Quality Status

3.1. Particulate Matter

Figure 3.1 shows the annual mean concentrations of PM_{10}. Both the exceedances of the annual limit values as well as stations where most likely the short-term (daily) limit value is exceeded are shown (the daily mean values may not exceed 50 µg/m^3 on more than 35 days per year). A statistical analysis of the monitoring data indicated that the daily PM_{10} limit value corresponds to an annual mean of 31 µg/m^3 (see e.g.: Working group on Particulate Matter 2004, Buijsman *et al.* 2005; Stedman *et al.* 2007). The map indicates that both limit values have been exceeded in many countries across Europe. The lowest concentration class corresponds to the WHO air quality guideline for PM_{10} of 20 µg/m^3 (WHO, 2006). At about 20% of the stations concentration is below this level although exceedances are observed in all countries.

For PM_{10}, the annual limit value was exceeded (red dots) particularly in Poland, Italy, Slovakia, several Balkan states, Turkey and a few urban regions elsewhere. The daily limit value was additionally exceeded (yellow dots) in several more cities in the mentioned countries as well as in many other countries including some Nordic countries. In the UK, exceedances were measured only in London.

The number of operational $PM_{2.5}$ stations has been increased again in 2010. The 2009 concentrations were higher than the annual target value to be met by 2010 (red and yellow dots) at several stations in Poland and Italy as well as at a few stations in other countries. The WHO AQG has been exceeded at more than 80% of the stations. A relatively large number of rural stations with concentrations below the AQG is seen on the Iberian Peninsula, Scandinavian countries and the United Kingdom.

The extent of exceedance of the annual limit values of PM is given in the frequency distribution graphs (Figure 3.2). For both size fractions exceedance of the limit values is observed at all types of stations with increasing numbers from rural to urban to traffic stations. Compliance with the WHO AQG is observed at 17% and 11% of the (sub)urban background stations measuring PM_{10} and $PM_{2.5}$, respectively.
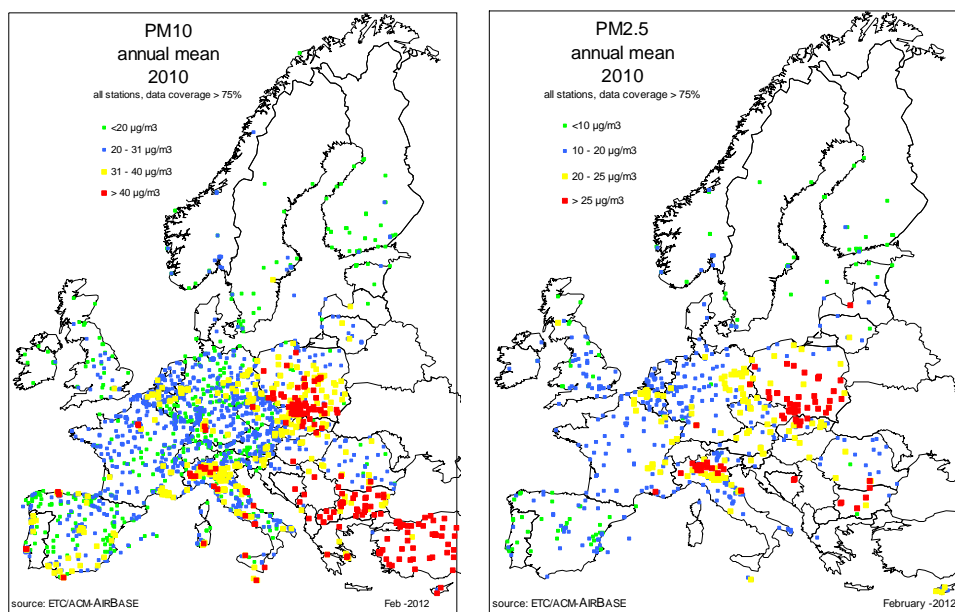
Figure 3.1. Left: Annual mean concentration map of PM_{10} (µg/m^3), 2010; the two highest concentration classes correspond to the annual limit value (40 µg/m^3) and to a statistically derived level (31 µg/m^3) corresponding to the short-term limit value. The lowest class corresponds to the WHO air quality guideline for PM_{10} of 20 µg/m^3. Right: Annual mean concentrations of $PM_{2.5}$, reference year 2010. The lowest class corresponds to the WHO air quality guideline for $PM_{2.5}$ of 10 µg/m^3.

Figure 3.2. Frequency distributions for annual mean values of PM_{10} and $PM_{2.5}$, data from all operational stations, reference year 2010. Concentrations have been compared to the WHO AQG (red line, 20 and 10 µg/m³ for PM_{10} and $PM_{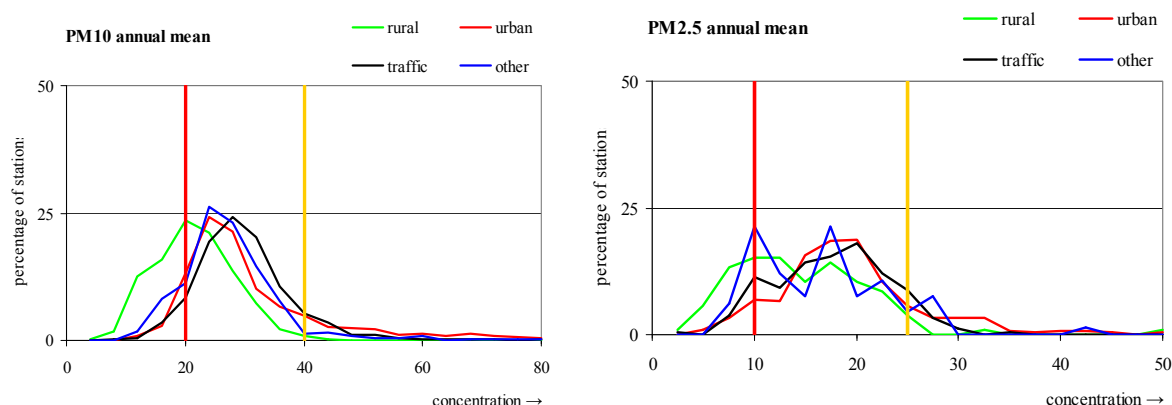2.5}$, respectively) and the EU limit values (orange line, 40 and 25 µg/m³ for PM_{10} and $PM_{2.5}$, respectively).
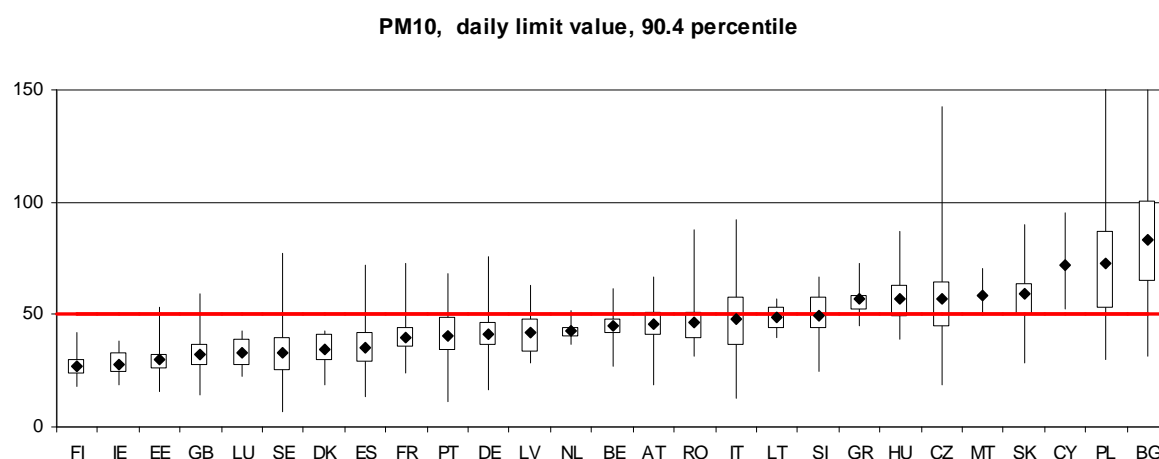

Figure 3.3. Box plots (all station types) of the 90.4 percentiles (based on daily mean values) of PM_{10}. The red line corresponds to the EU limit value, EU Member states only, reference year 2010.

The PM_{10} daily limit value is more frequently exceeded than the annual limit value. Figure 3.3 shows for all Member States box plots of the 90.41 percentile of daily mean values. As 35 exceedances of the limit value are allowed, a 90.41 percentile value of more than 50 µg/m³ indicates a non-attainment situation. Figure 3.3 clearly indicates that violation of the daily limit value is observed in 23 Member States on one or more stations.

At most of the stations operational during the past 10 years (2001-2010) there is a tendency that annual mean concentrations decrease with 0 – 1 µg/m³ per year (Figure 3.4). However, at a large fraction of the stations this decreasing trend is not significant, see the example for (sub)urban traffic stations presented in Figure 3.4. A significant downward trend is estimated for half of the stations; at the traffic hot-spot location a slightly larger trend is estimated than averaged for all stations. More details on the applied trend model can be found in Annex A. In the course of 2006 a nation-wide system was introduced in France to correct the PM_{10} measurements from non-reference measuring configurations. In the Mann-Kendall analyses the French data prior to 2007 have been corrected using station-type dependent factors (de Leeuw and Fiala, 2009).

The air quality directive (2008/50/EC) introduced an additional $PM_{2.5}$ objective targeting the exposure of the population to fine particles. These objectives are set at the national level and are based on the average exposure indicator (AEI). The AEI is determined as a three-year running annual
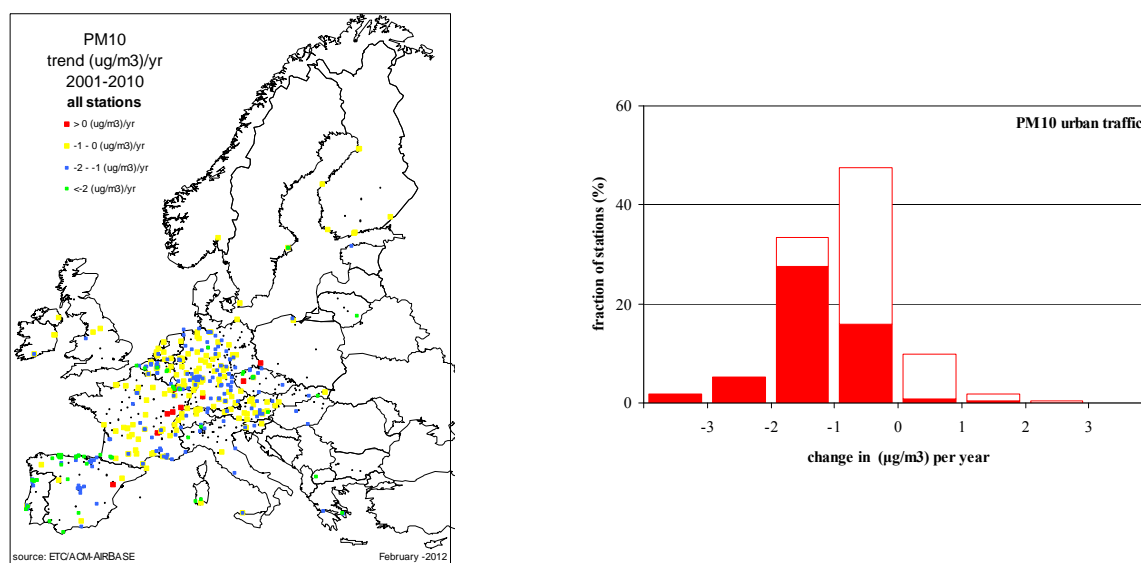
Figure 3.4. Left: spatial distribution and estimated trend at stations used in the trend analysis of PM₁₀
concentrations; stations where no significant trend is observed are indicated with a small black dot, period
2001-2010; right: frequency distribution of estimated change (in µg/m³ per year) at (sub)urban traffic stations;
closed bars refer to stations having a significant trend, open bars to stations having a non-significant trend.

mean concentration measured at a selected set of stations in urban background locations
throughout the territory of a Member State. The AEI reflects the $PM_{2.5}$-exposure of the general
(urban) population.

In the air quality reporting questionnaire (EC, 2004b) 14 Member States[6] provided information on
stations and measurement configurations selected for determination of the AEI. In the 2010
questionnaire, 10 Member States have reported an AEI, see Figure 3.5. As an alternative estimate of
the AEI we have calculated here the three-year running mean (2008-2010) as the mean of the annual
averaged concentration over all operational (sub)urban background stations in each individual year.
The approximated AEI (*Figure 3.5*) is not based on a stable set of stations. For a number of countries
results are based on two years only. In general, the officially reported AEI, based on a dedicated set
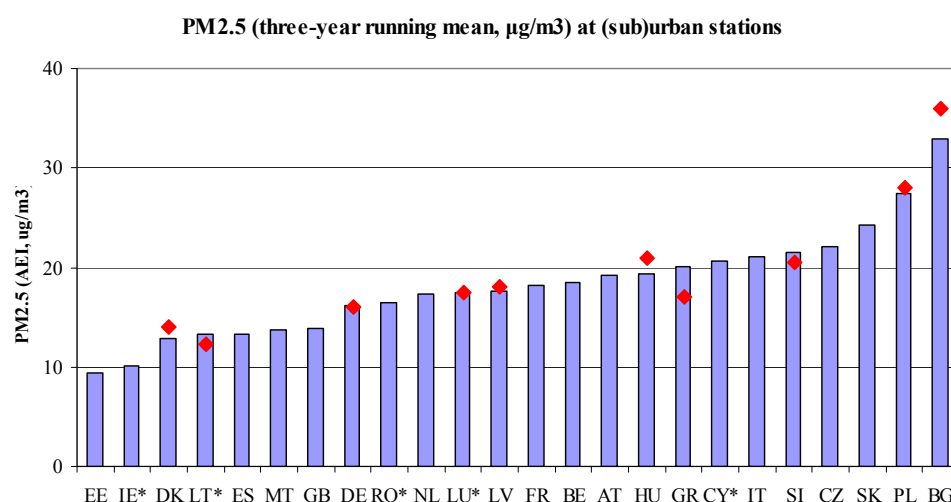
Figure 3.5. Average Exposure Indicator, three-year running mean (2008-2010) over all operational
(sub)urban background stations. Results for countries marked with an asterisk are based on 2009-2010 data
only. The AEI as reported under the air quality questionnaire decision (EC, 2004b) is given by the red dots.

---

[6] Preliminary data, based on information available per 10 January 2012 as reported by the MS under the air
quality questionnaire decision (EC, 2004b).

of (sub)urban station agrees well with the AEI estimated here on the basis of all operational (sub)urban background stations. Figure 3.5 indicates that in 8 Member States current urban concentrations are above 20 µg/m^3, the level legally binding in 2015.

The aerosol plume resulting from the eruption of the volcano Eyjafjallajökull in Iceland in April and May 2010 had a large impact on the flight traffic in Europe. During several days in mid April the plume caused a nearly complete closure of airports in Central Europe. During the last year a number of papers describing the influence of the Eyjafjallajökull on the air quality have been published[7]. Although the plume has been observed at altitudes of 6-7 km, the impact of the volcanic emissions has also been recorded at measurement stations at ground level.

Figure 3.6 show the hourly PM_{10} and SO_2 concentration at stations in Belgium and Germany together with backward trajectories calculated using the Hysplit[8]-model (Draxler and Rolph, 2012; Rolph, 2012). On the stations Schauinsland (DEUB004) and Engis (BETR240) there is both an increase in PM_{10}

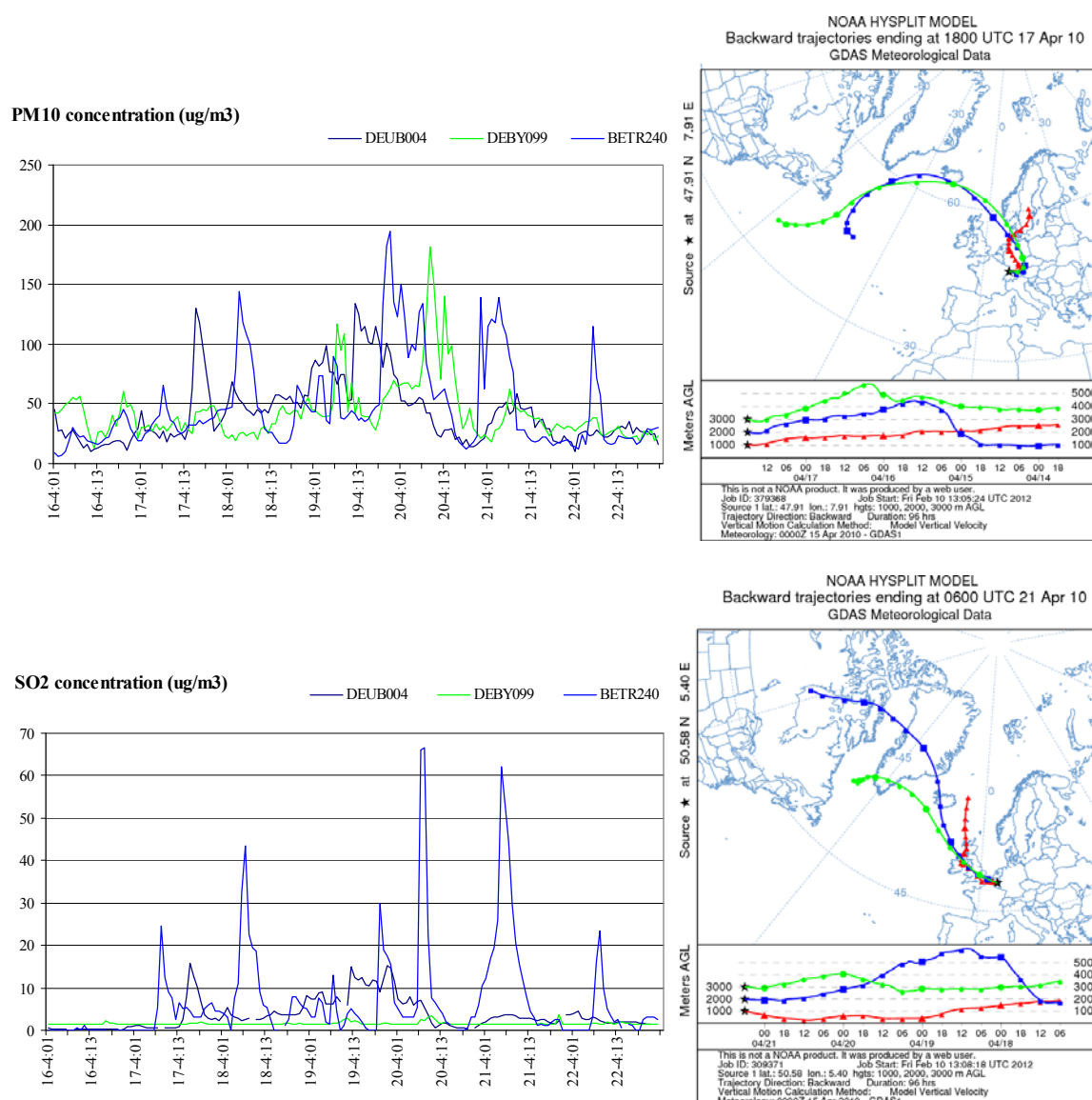*Figure 3.6. Hourly PM_{10} (top) and SO_2 (bottom) concentrations at the stations DEUB004 (Schauinsland), DEBY0099 (Augsburg) and BETR240 (Engis) during the first volcanic ash episode. Backward trajectories arriving DEB004 (17 April, 18:00 UT, top) and in BETR240 (21 April 06:00 UT, bottom).*

---

[7] see annex B for an (incomplete) overview of recently published papers on the Eyjafjallajökull eruption.

and SO$_2$ concentrations; on the stations Augsbürg (DEBY099), however, no increased SO$_2$ levels are observed. The high peaks in PM$_{10}$ concentrations coincide with the arrivals of the backward trajectories in Schauinsland (top panel) on 17 April 18:00 UT and in Engis on 21 April 6:00 UT. This figure gives a few examples on how the information in AirBase could be used to describe these volcanic ash episodes; for a more in depth discussion we like to refer to the papers listed in Annex B.

Whereas for northern Europe the PM$_{10}$ concentrations as shown in Figure 3.6 are rather exceptional, similar concentrations are usually recorded every year due to African dust intrusions. In Cyprus daily mean concentrations measured at the background station Agia Marina has exceeded 1000 µg/m^3 in one case but each year daily levels of 200 µg/m^3 or more are measured during several days per year, see Figure 3.7. The backward trajectories show that concentrations exceeding 100 µg/m^3 are associated with air parcels originating in the Sahara or the arid regions in the Middle East. Air masses tarvelling over (western)Europe are associated with concentrations below 50 µg/m^3.
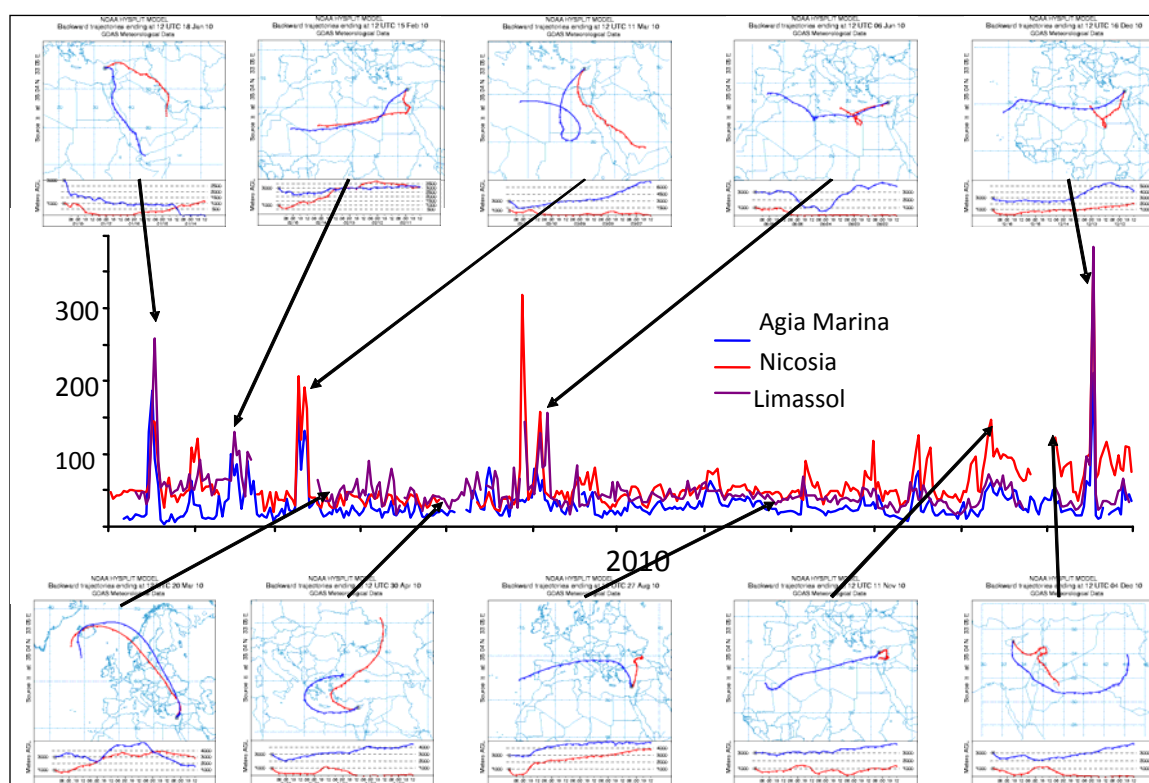
Figure 3.7. Daily PM10 concentration measured at three stations in Cyprus in 2010. For a selected number of days backward trajectories have been calculated showing the origin of the air parcels arriving in Cyprus. Source: Annual reporting on ambient air quality (2004/461/EC), national report Cyprus, 2010 data.

3.2.   Ozone

Figure 3.8 shows the annual mean values of the maximum concentrations of O$_3$. The WHO Air quality Guideline and the EU target values are both maximum daily running 8-hour mean. Note, however, that the map show the annual mean value while the WHO AQG is expressed in terms of the maximum value and the EU TV as 25 allowable exceedances of a level of 120 µg/m^3. A map showing the maximum concentrations is very sensitive to local and meteorological conditions; a more robust quantity like the annual mean concentration is more representative for the ozone climatology over Europe.

---

[8] The authors acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.php) used in this publication.

Ozone concentrations show a clear north-south gradient with the highest concentrations in the Mediterranean countries. Several reasons may contribute to this: higher insolation, higher biogenic emissions in summertime, intensive recirculation of air masses, and a lower deposition of ozone under hot and dry conditions.

In contrast to the other pollutant the ozone levels are generally the highest at rural locations. Reason for this is that at short distances from NO_x sources – as is the case for urban and traffic stations – the ozone is chemically quenched by the freshly emitted NO_x. The higher the NO_x concentrations (i.e. the closer to traffic emissions) the lower ozone concentrations are due to a more complete quenching. Ozone background levels further increase with altitude, high levels are also observed at mountain stations. A slight increase in O_3 levels is detected in a number of urban sites probably due to reduction of the NO concentrations.

The extent of exceedance of the ozone reference values is given in the frequency distribution graphs (Figure 3.9). Compliance with the WHO AQG set for the protection of human health is observed at 5 %, 9 % and 24% of the rural, (sub)urban background and traffic stations, respectively. Although the EU target value (120 $\mu g/m^3$, 25 exceedances allowed) is less ambitious than the WHO AQG, non-attainment situations are widely found in most of the Member States as is shown by the box plots given in Figure 3.10. In (sub)urban areas the observed levels are in compliance with the target value at about 75% of the background stations.

In addition to a reference levels for the protection of human health set by WHO, within the UN-ECE CLRTAP convention a critical level for the protection of forests has been defined. This critical level (set at 10 000 $(\mu g/m^3)$.h) is defined in terms of an AOT40 (the accumulated dose of ozone over a threshold of 40 ppb, equivalent to 80 $\mu g/m^3$). The accumulation period is the six summer months. The frequency distribution, Figure 3.9, calculated for rural stations only, shows that at nearly all rural stations current concentrations are above this critical level. The few stations which are in compliance are mostly located in NW Europe. In the Air Quality Directive 2008/50/EC an ozone target value has been set for the protection of vegetation; this value, also defined as AOT40 has been set to 18000 $(\mu g/m^3)$.h. In the AQ Directive the accumulation period is defined as the growing season for crops
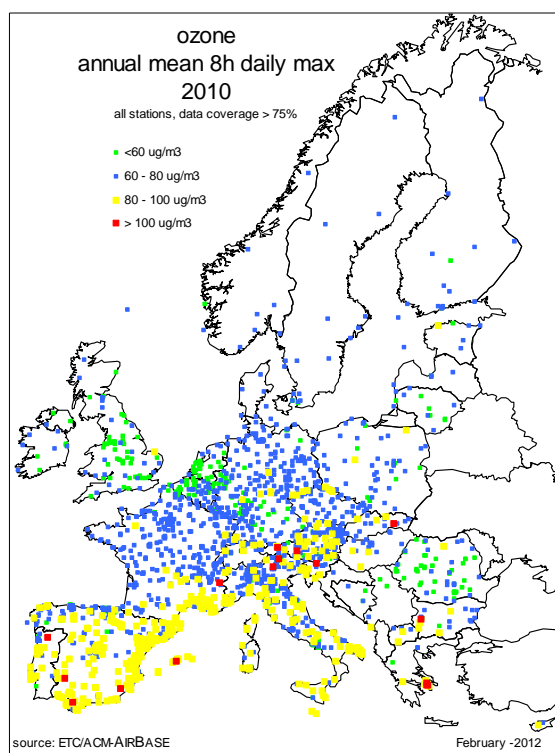

Figure 3.8. Annual mean value of the maximum daily 8-hour mean value of ozone, 2010.
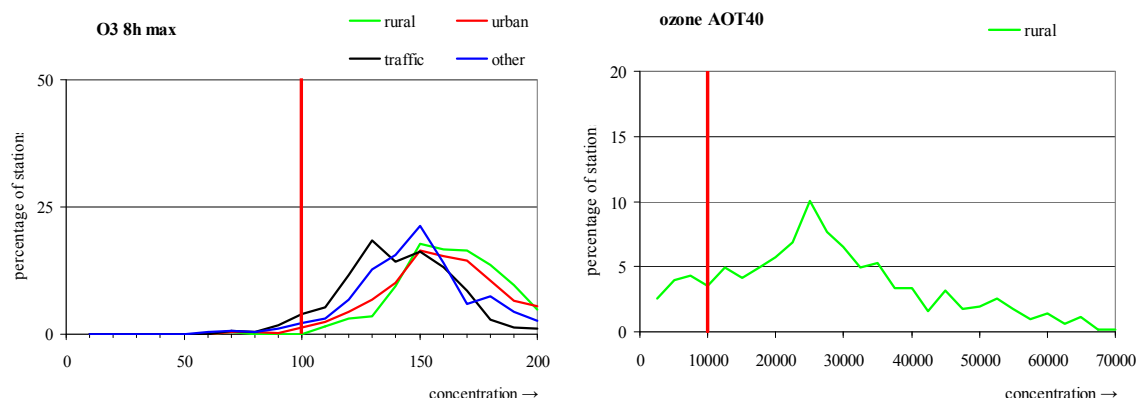
Figure 3.9. Frequency distributions for the maximum running 8 hour mean value of ozone (left) , data from all operational stations, and AOT40 (right, accumulated over April-September), data for rural stations only, reference year 2010. Data have been compared to the WHO AQG and UNECE –CLRTAP critical level.

(May-July). The shorter period and the higher value obviously resulted in a substantially lower number of non-compliance situations

Trends in ozone concentrations are small, generally not-significant and may be different for the different station types and for different indicators (Mol et al, 2011). The highest concentrations tend to decrease. In summer 2011 the number of exceedances of the ozone information threshold (hourly mean concentration exceeding 180 µg/m^3) and the long-term objective for the protection of human health (maximum running 8 hour mean value not exceeding 120 µg/m^3) was the lowest since comprehensive European-wide data reporting started in 1997 (EEA, 2012, to be published).

The temporal changes of the annual mean of the maximum daily 8-hour mean values over the period 2001-2010 are shown in Figure 3.11. The map and frequency distributions show that significant trends are only observed at a small fraction of the stations. At 27% of the rural stations a significant decreasing trend is observed. On (sub)urban background stations a significant trend is observed at not more than 15% of the stations; in general ozone concentrations are decreasing at the urban stations although at a small fraction (3.7% of the 614 urban stations included in the analysis) concentrations are increasing. There are 153 urban traffic stations included in the analysis; at 28% of these the trend is significant: decreasing at 12 and increasing at 31 stations. The increasing ozone levels is mainly attributed to a reduced quenching by NO$_x$ as a result of the decrease in traffic NO$_x$ emissions.

Most of the stations having a large positive trend are located in the Iberian Peninsula. Seven out of
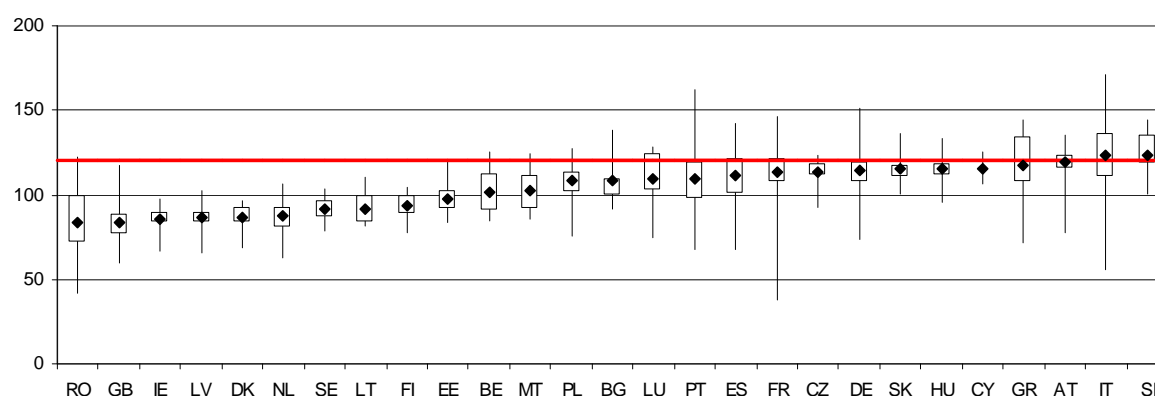
Figure 3.10. Box plots (all station types) of the 93.15 percentiles (based on daily maximum values) of O$_3$. The red line corresponds to the EU target value, EU Member states only, reference year 2010.

the eleven stations are classified as being a traffic station, the others are urban or industrial stations. This might indicate again the impact of reducing NO_x traffic emissions but a clear explanation has not been given (X. Querol, personal communication 2012)

The health related target value (maximum daily running 8-hour mean, 93.2 percentile) which is more representative for the higher ozone levels, shows a slightly different picture: a significant trend is estimated at less than 19% of the stations. However, when a significant trend is observed at urban or rural stations it is downward. At traffic stations a mixed pattern is seen: at 10 stations levels are significantly increasing, at 19 decreasing.
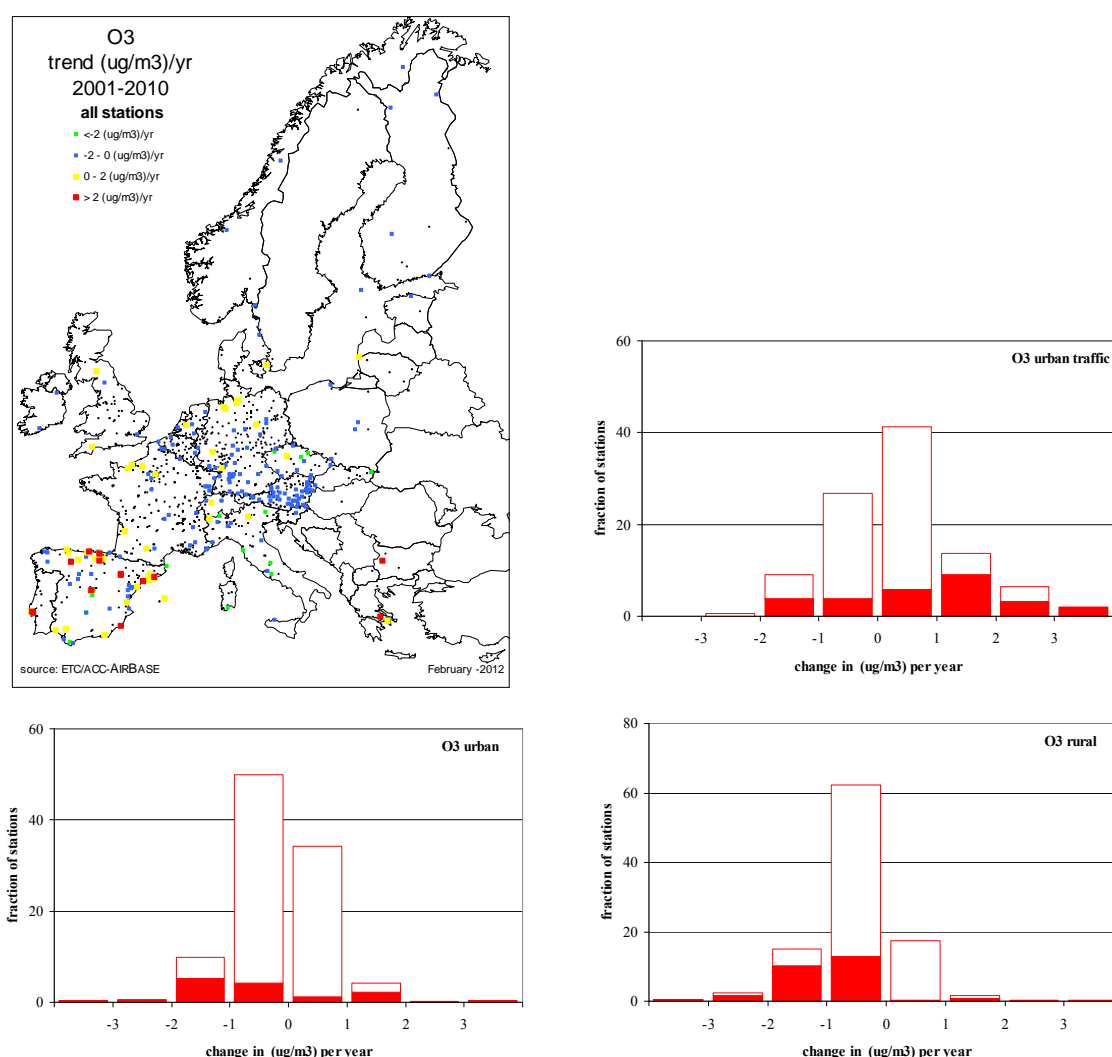
Figure 3.11. Spatial distribution and estimated trend at stations used in the trend analysis of the annual mean of the maximum daily 8-hour mean ozone values; stations where no significant trend is observed are indicated with a small black dot, period 2001-2010. Frequency distribution of the estimated change per year (in µg/m³ per year) for each of the station types. Closed bars refer to stations having a significant trend, open bars to stations having a non-significant trend.

3.3.   Nitrogen oxides

The annual mean NO_2 concentrations are given in Figure 3.12. It is evident that the WHO AQG of 40 µg/m^3 (which is similar to the EU limit value) has been widely exceeded in Europe. Concentrations of 50-100 µg/m^3 (25% up to 150% above the AQG) are observed, most frequently at traffic stations.
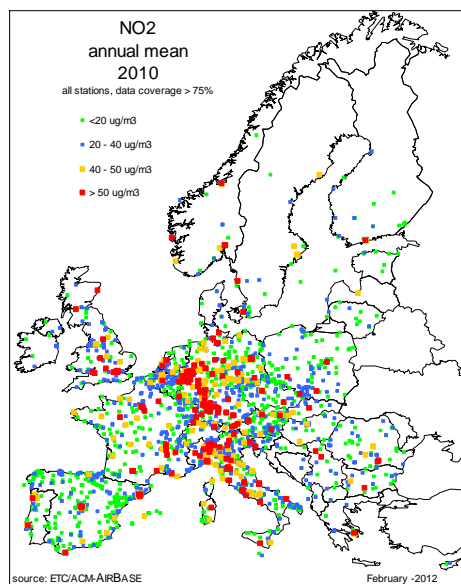
Figure 3.12. Annual mean concentration map of NO$_2$ (µg/m^3); the two highest concentration classes correspond to the WHO AQG (40 µg/m^3, equal to the EU limit value) and more than 25% above the AQG (> 50 µg/m^3), respectively; reference period 2010.

The different concentration levels at rural, urban and traffic stations are clearly seen in the frequency distribution graph (Figure 3.13): while the AQG is not exceeded in the rural background, it is exceeded at 49% of the traffic stations with an observed concentration of more than 100 µg/m^3 at stations in Florence and Stuttgart. At 41 (sub)urban stations (4%) an exceedance of the AQG is observed.

Figure 3.14 shows in more detail the situation in the EU Member States. In 22 of the 27 Member States the limit value has been exceeded at one or more stations. The information submitted under the AQ reporting questionnaire confirms this[6]: one third of the AQ management zones report an exceedance of the NO_2 limit value. Although the exceedances might be limited to one or several hot spots within a zone, the total population living in these zones and potentially exposed to
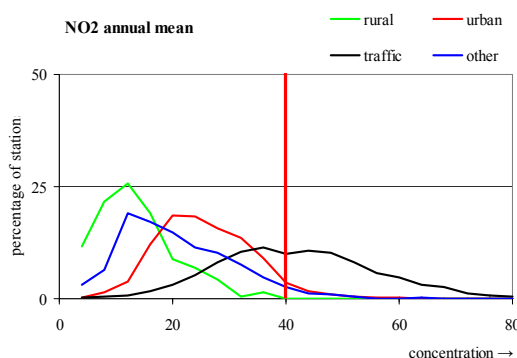
Figure 3.13. Frequency distribution for the annual mean value of NO$_2$, data from all operational stations, reference year 2010. Data have been compared to the WHO AQG (40 µg/m^3) which is equal to the EU annual limit value.

NO2, annual limit value

Figure 3.14. Box plots (all station types) of the annual mean values of NO$_2$. The red line corresponds to the EU limit value of 40 µg/m^3, EU Member states only, reference year 2010.

concentrations above the limit value is estimated to more than 220 million (Jimmink et al, 2012).The hourly limit value of NO$_2$ (200 µg/m^3, not to be exceeded during more than 18 hours) is less stringent with exceedances at about 1 and 4% of the urban and traffic stations located in EU Member States.

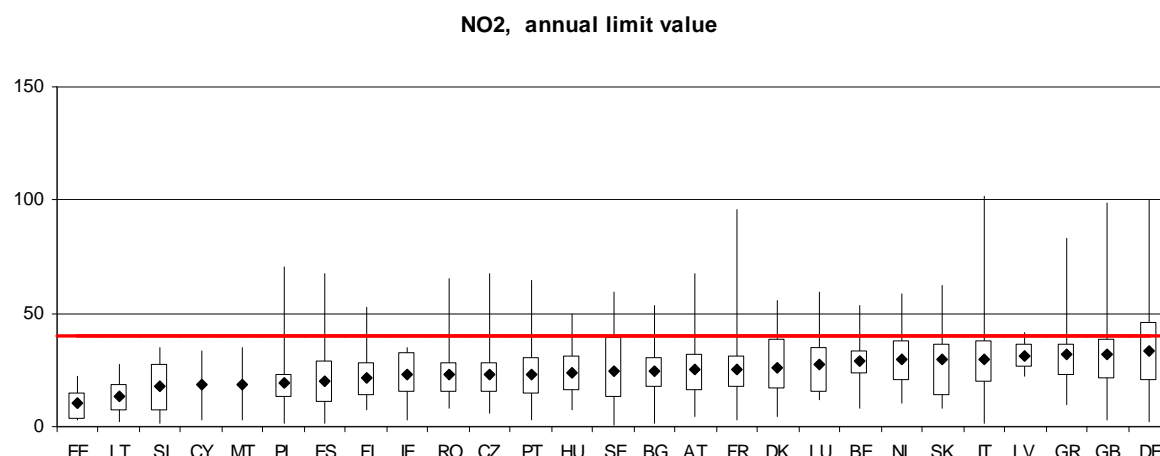Exceedances of the annual limit value are rather persistent: within the EU27, at 12% (200 out of 1684) of the stations operational in the 5-year period 2006-2010 showed each year an exceedance. Over the period 2005-2009 similar numbers were found: at about 11% (190 out of 1660) of the stations the limit value is uninterruptedly exceeded. The long-lasting exceedances are mostly observed at traffic stations. The impact of an increasing number of diesel cars leading to an increased fraction of direct NO$_2$ emissions might counteract the effect of reductions in the NO$_x$ emissions from road transport. A more extensive discussion on the NO$_2$ hotspot situations is given by Guerreiro et al (2011).

The change in annual mean NO$_2$ concentration over the period 2001-2010 is summarized in Figure 3.15. A consistent set of 1467 stations has been included in the trend analysis. At about one third of these stations a significant trend which is in general downwards, has been observed. In the consistent set 178 stations are included where the NO$_2$ limit value is exceeded in 2010. At 126 of these non-compliance stations the concentrations have significantly changed during the past 10 years. Of the remaining 52 stations, 33 stations show a significant downward trend; at 19 stations concentration are increasing.

At the more than 200 stations an annual mean concentration of more than 50 µg/m^3 has been observed in 2010. If the above trend is representative for these hotspot stations and if the trend remains similar during the coming years, it might take more than a decade before the annual limit value (40 µg/m^3) will be met at these hotspot locations.
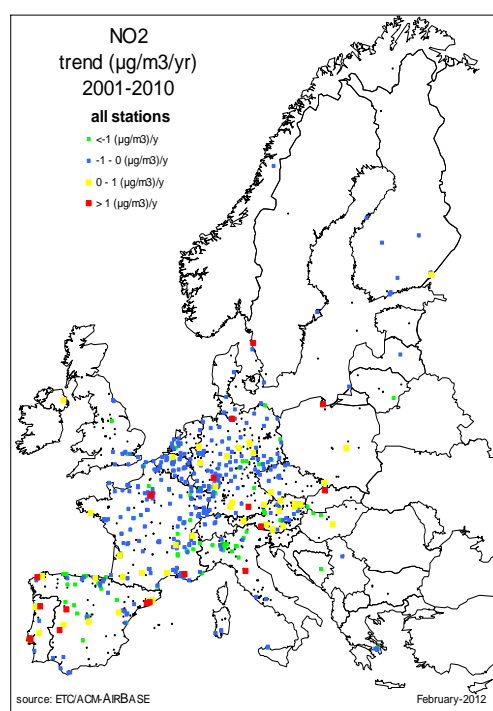

Figure 3.15. Spatial distribution and estimated trend at stations used in the trend analysis of the annual NO$_2$ concentrations; stations where no significant trend is observed are indicated with a small black dot, period 2001-2010.

3.4.   Sulphur dioxide

The annual mean SO_2 concentrations are given in *Figure 3.16*; like in previous years the highest concentrations are observed in the West Balkan countries and Turkey. The EU limit value set for the protection of vegetation (20 µg/m^3 as annual mean) has been exceeded at 1.1% of the stations in EU Member States. However, none of the exceedance stations are classified as rural background; the vegetation limit value might not be applicable here. As emissions tend to be higher and dispersion condition are worse during winter periods, the concentrations during the winter 2009/2010 are on the average slightly higher than those during the calendar year 2010. The more stringent limit value for the protection of vegetation set for a winter period (20 µg/m^3) has not been exceeded at any rural station within the EU.

The WHO AQG set for the protection of human health is 20 µg/m^3 as a daily average is widely exceeded at all type of stations (see Figure 3.17). The WHO interim target (IT-1) of 125 µg/m^3 as a daily average corresponds to the EU daily limit value although for the latter 3 exceedances per year is allowed. A limited number of exceedances of the EU daily limit value are seen in eastern European MS (Figure 3.18). As three exceedances per year are allowed, a 99.18 percentile of more than 125 µg/m^3 indicates a non-attainment situation. In three air quality management zones SO_2 concentrations are above the daily limit value; in two of them the hourly limit value has also been exceeded. In one additional Polish zone also non-attainment of the hourly limit value has been observed.
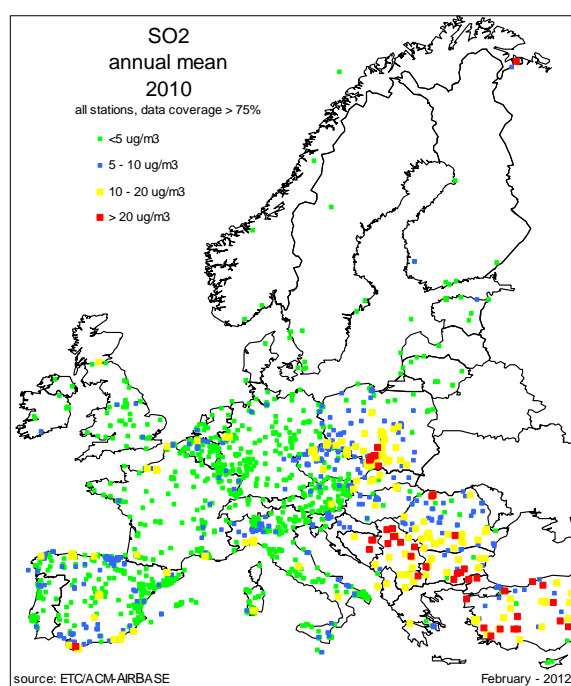
Figure 3.16. Annual mean concentration map of SO$_2$ (µg/m^3); the highest concentration class correspond to the EU limit value of 20 µg/m^3 set for the protection of vegetation; reference period 2010.
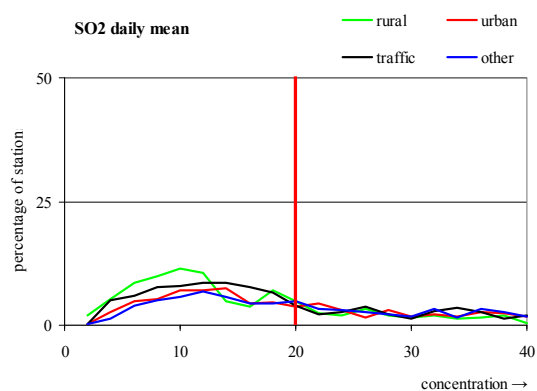
Figure 3.17. Frequency distribution for the daily mean value of SO$_2$, data from all operational stations, reference year 2010. Data have been compared to the WHO AQG (20 µg/m^3).

SO2, daily limit value, 99.18 percentile
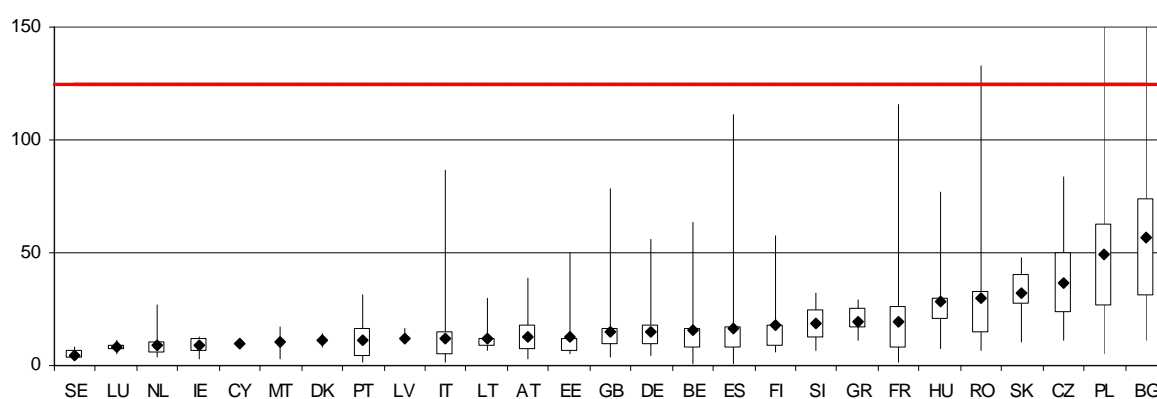
Figure 3.18. Box plots (all station types) of the 99.18 percentile value of SO$_2$ daily mean values. The red line corresponds to the EU limit value of 125 µg/m^3, EU Member states only, reference year 2010.

The SO$_2$ concentrations show a steady decrease over the period 2001-2010 (see *Figure 3.19*). At all station types the concentrations decreased by about 40% over the last 10 years. At nearly all (sub)urban background and traffic stations a significant trend is observed.

During the most recent years, the concentration at traffic stations is on average only slightly higher than at the (sub)urban background stations suggesting that the contribution to SO$_2$ emissions from road traffic is small.
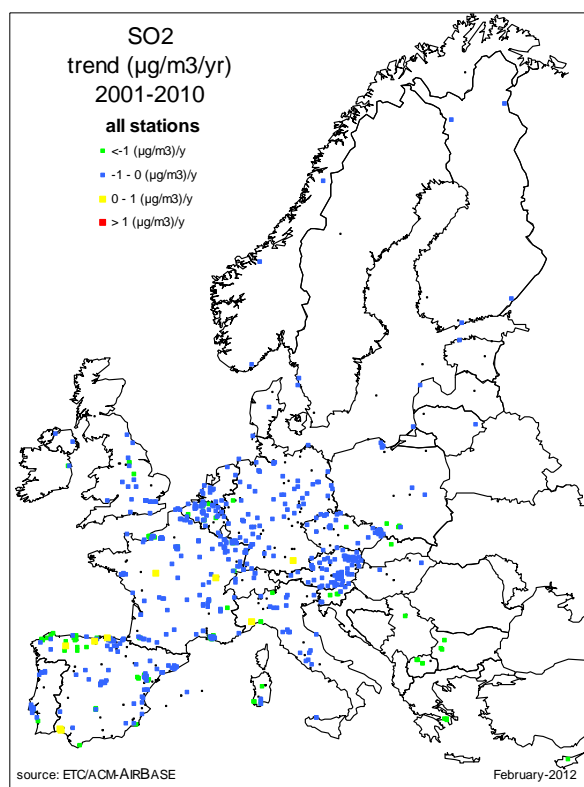
Figure 3.19. Spatial distribution and estimated trend at stations used in the trend analysis of the annual SO₂ concentrations; stations where no significant trend is observed are indicated with a small black dot, period 2001-2010.

3.5.   Carbon monoxide

The annual averages of the daily maximum of 8-hour means show elevated levels in the same regions, see Figure 3.20. Note that not the maximum value is plotted but the more robust annual mean value of daily maximum 8-hour mean values.

The WHO has set as AQG for the protection of human health a maximum daily 8-hour mean values not to exceed 10 mg/m^3; the EU limit value is equivalent to this AQG. The frequency distribution given in Figure 3.21 indicates exceedances at a very small number of stations. The box plots (Figure 3.22) shows that in 5 Member States the limit value has been exceeded. The seven stations where this occurred are all traffic, industrial or background urban stations. Note that the maximum value is sensitive to actual meteorological conditions and may therefore show large year-to-year fluctuations. It should also be considered that CO – more than any of the other pollutants – is typically measured at traffic stations; nearly 50% of the stations are traffic stations. Figure 3.22 is therefore more representative for hot-spot situation. By comparison, the corresponding ozone figure (Figure 3.10) will be more representative for the exposure in urban areas as nearly 50% of the ozone stations is labelled as (sub)urban background.

In contrast to the situation for the NO₂ annual limit value, there is no persistency in CO exceedance situations. In the last five years, the limit value was violated in three years at two stations; at 6 additional stations the exceedance occurred during two years.

The steady decrease in CO concentrations found earlier (Mol et al, 2011) continues during the period 2001—2010. More than 80% of (sub)urban background and traffic stations show a downward trend which is significant at 65% and 80%, of the urban and traffic stations respectively. At the limited

number of rural stations (18 in total) trends are less clear. Uncertainties are introduced by concentrations around and below the detection limit of the monitors and by a relatively large contribution of the hemispheric background. The hemispheric background concentration of 0.14 mg/m3, (averaged value over 2007-2009) measured at Mace Head, Ireland (WDCGG, 2011) contributes at least 50% to the averaged CO concentrations at rural background locations.

Figure 3.20. Annual mean concentration of the maximum daily 8-hour mean value of CO (mg/m3), reference period 2010.

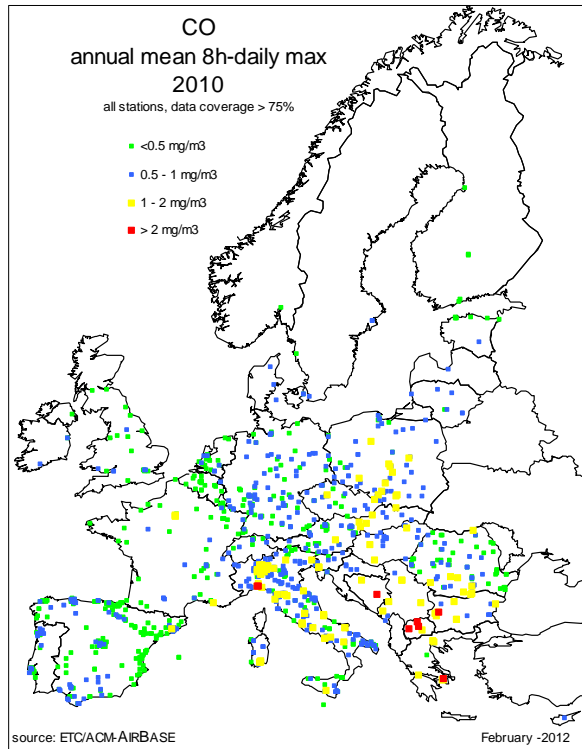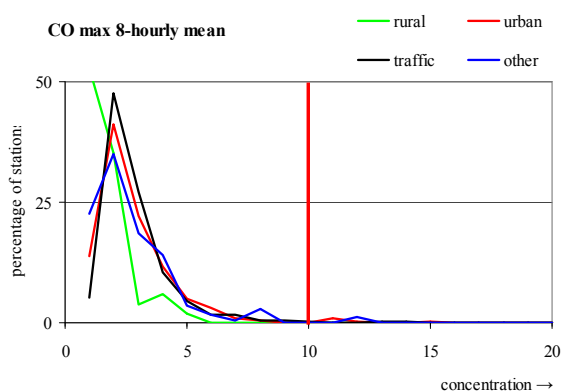*Figure 3.21. Frequency distribution for the maximum daily 8-hour mean values of CO, data from all operational stations, reference year 2010. Data have been compared to the WHO AQG and EU limit value (both 10 mg/m^3).*
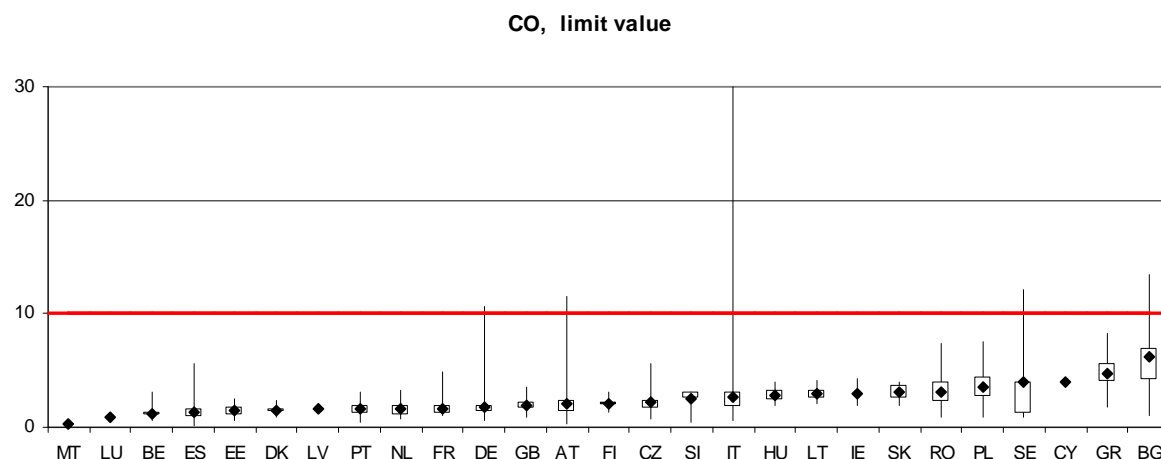
CO, limit value

Figure 3.22. Box plots (all station types) of the maximum daily 8-hour mean value of CO. The red line corresponds to the EU limit value of 10 mg/m³, EU Member states only, reference year 2010.

3.6. Benzene and benzo(a)pyrene

Benzene is carcinogenic to humans and therefore a safe level of exposure can not be set. The WHO has not recommended a guideline value. The WHO (2000) estimated the excess lifetime risk of leukaemia at an air concentration of 1 μg/m³ to be 6 x 10^{-6}. The acceptance that the upper limit of an additional lifetime risk should be less than 1 x 10^{-5} would suggest an ambient air quality reference value for annual mean concentration of benzene of 1.7 μg/m³. Note that this might be an upper estimate; in general ~ 1 x 10^{-6} is seen as an acceptable risk level (RIVM, 2003). The EU has set an annual limit value of 5 μg/m³; this level corresponds to an excess lifetime risk of 3 x 10^{-5}.

In the spatial and frequency distribution of the observed benzene concentrations, both the WHO-based reference level as well as the EU limit value is given (Figure 3.23). There are hardly any exceedances of the EU limit value but the WHO-based reference value has widely been exceeded, in particular at traffic and (sub)urban background sites.

Benzene is measured at a relatively small number of stations. Annual mean concentrations are at many locations below the lower assessment threshold of 2 μg/m³ (Barrett *et al.* 2008). When concentrations are below the lower assessment threshold the air quality can be assessed by means of indicative or discontinuous measurements. For discontinuous measurements data coverage lower than 75% will not largely increase the uncertainties in the annual mean values as long as the measurements take place randomly spread over the year (Working group on benzene, 1998; see also Chapter 6). For this reason we have applied here a data coverage criterion of more than 50%.

In the past 10 years the benzene annual mean have been decreased (*Figure 3.24)*. The highest concentrations are measured at traffic stations. Benzene in gasoline is still one of the most important sources, but there is a steady decrease until 2007 when concentrations seem to stabilize. A similar but less outspoken pattern is seen at the urban stations. Whether a similar stabilisation is also seen in the benzene emissions is not clear; benzene is not included as an individual pollutant in the European emissions inventories.
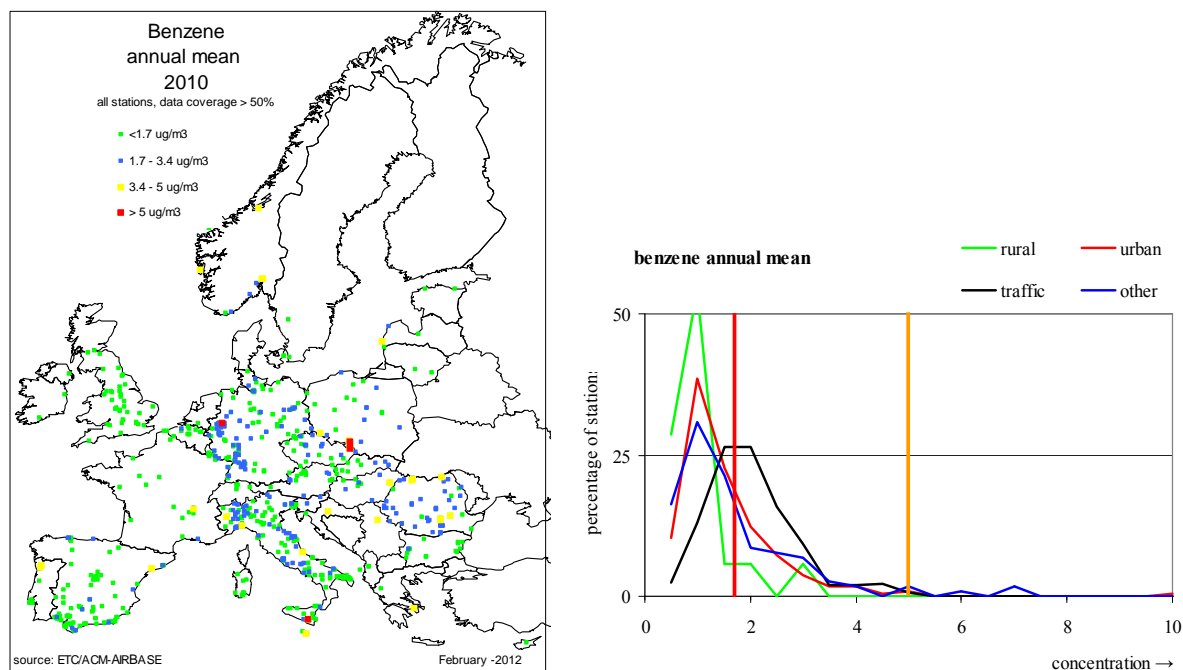
Figure 3.23. Left: annual mean concentration of benzene (µg/m³); right: frequency distribution for the annual mean concentration of benzene, data from all operational stations. Data have been compared to a reference level having an excess lifetime risk of leukaemia of 1 x 10⁻⁵ (1.7 µg/m³) and the EU annual limit value (5 µg/m³); reference period 2010.

Polycyclic Aromatic Hydrocarbons: benzo(a)pyrene

No specific guideline can be recommended for PAH as such in air (WHO, 2000). These compounds are typically constituents of complex mixtures. Based on occupational epidemiology data which should serve as the basis for the risk estimate for exposure to ambient levels, a unit risk for B(a)P as
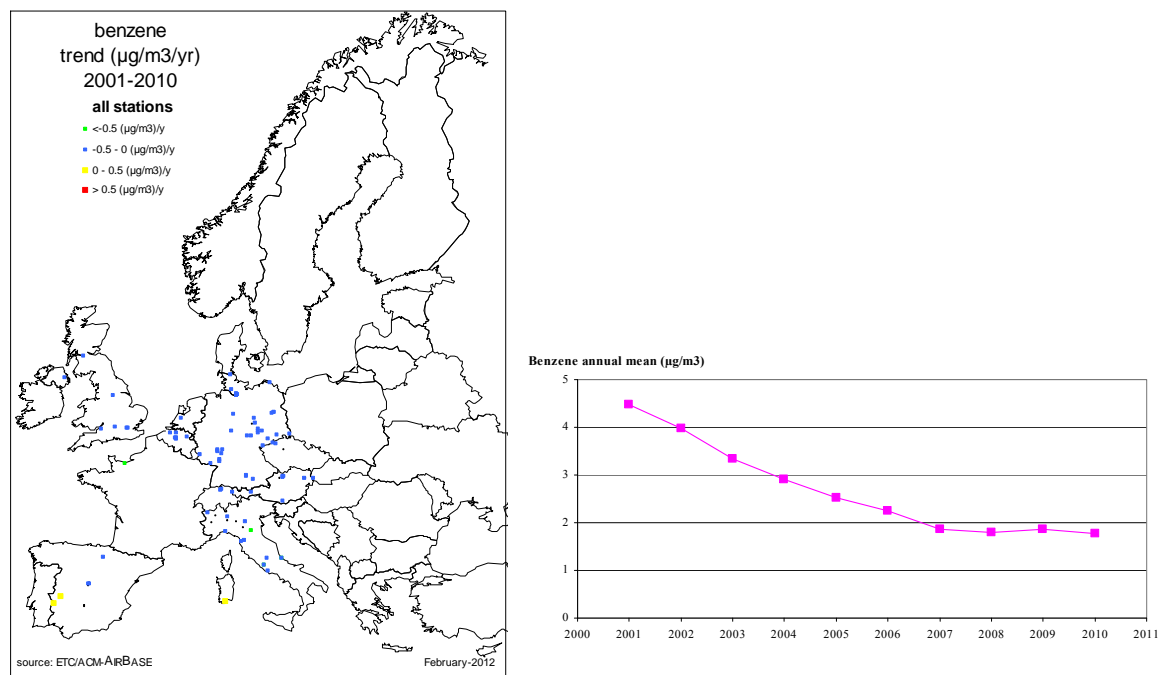
Figure 3.24. Spatial distribution and estimated trend at stations used in the trend analysis of the annual benzene concentrations; stations where no significant trend is observed are indicated with a small black dot; trend in annual mean benzene concentrations at traffic stations (period 2001-2010; a consistent set of stations is used).

indicator for the ambient PAH mixture is estimated to be 8.7 x 10^{-5} per ng/m^3. The corresponding reference level of B(a)P producing excess lifetime cancer risk of 1 x 10^{-5} is 0.12 ng/m$^{3.}$ The map and frequency distribution of B(a)P measurements (Figure 3.25) indicates that the reference level is widely exceeded. The reference level is exceeded at 93% of the stations, the EU target value (1 ng/m^3 as annual average to be met in 2013) at 38% of the monitoring points. This was the case mainly at (sub)urban background stations and, to a lesser extent, at the other stations types (rural, traffic and industrial stations). There is a concentration of impact in central and eastern Europe (NE-SW corridor from the Baltic States, over Poland, Czech Republic, Slovakia, Hungary and Austria, Slovenia, the Po Valley) although exceedances of the EU target value are also observed in the UK (Midlands, Northern Ireland), Ireland, the German Ruhr area and Bulgaria (see *Figure 3.25*).

The wide-spread observed exceedances are in agreement with the national reports under the Air Quality Directives[6], where, in addition to the MS mentioned above, France and Greece report exceedance of the target value in one or more zones. The assessment for Greece is based on modelling. The exceedances in France are based on monitoring data; these data are, however, not submitted under the Exchange of Information decision and therefore not available in AirBase. The total population living in zones reporting an exceedance and potentially exposed to B(a)P concentrations above the target value is estimated as 105 million persons (Jimmink et al, 2012).

The exceedances of the EU target value are persistent: at 30% of the stations reporting an exceedance in 2010, the non-attainment situation continued at least for the last three years (2008-2010).

3.7.   Heavy metals

Barrett et al. (2008) reviewed the concentrations of lead and the heavy metals covered by the Fourth Daughter Directive 2004/107/EC (EC, 2004b), i.e. arsenic, cadmium, and nickel pointed to the little availability of concentration measurements. As concentrations of these pollutants are frequently below the lower assessment threshold (LAT), techniques other than monitoring can be used for
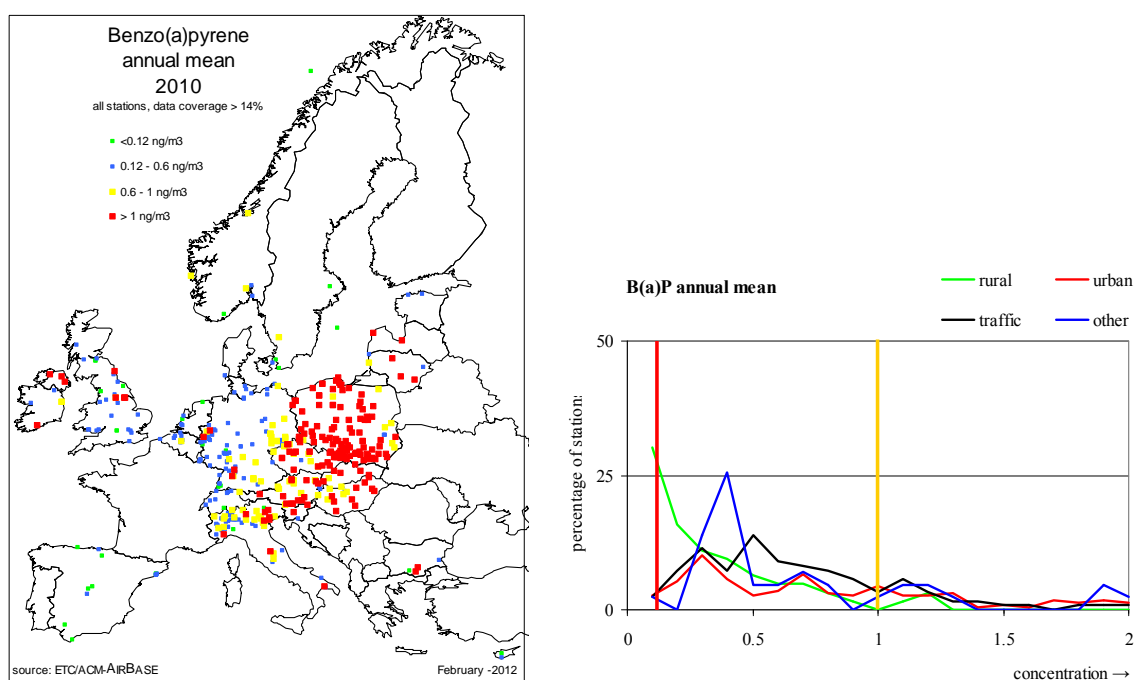
Figure 3.25. Annual mean concentration of benzo(a)pyrene (ng/m3), Frequency distribution for the annual mean concentration of benzo(a)pyrene, data from all operational stations, reference year 2010. Data have been compared to a reference level of 0.12 ng/m^3 (see text) and the EU target value (1 ng/m^3).

assessing air quality. This might be the reason why these pollutants are reported for a relatively small number of stations. Following the data quality objectives set in EU legislation, for indicative measurements a criterion on data coverage of 14 % is applied here on the heavy metal data. A problem in analysing the data of these pollutants is that it is not always certain (from the data made available by the countries) whether the heavy metals have been measured on the PM_{10} fraction or on another (undefined) size fraction (Mol et al, 2011).

Table 3.1 lists the EU limit or target values set for the protection of human health. The reference values given in this table are based on the assessments of WHO (2000). Arsenic and nickel compounds are human carcinogens and no safe level for inhalation exposure can be recommended. The given values correspond to an excess lifetime risk level of 10^{-5}.
The finding of renal effects of cadmium in area contaminated by past emissions indicates that the cadmium body burden of the general population in some parts of Europe cannot be further increased without endangering renal function. To prevent any further increase of cadmium in agricultural soils likely to increase the dietary intake of future generations, a guideline of 5 ng/m3 is established (WHO, 2000). For lead WHO (2000) has recommended an AQG of 0.5 $\mu g/m^3$.

Table.3.1. Limit and target values for the protection of human health as set by the European Union compared with reference value based on WHO reports.

pollutant	EU limit or target value (a)	Reference value (b)
arsenic	6 ng/m^3	6.6 ng/m^3
cadmium	5 ng/m^3	5 ng/m^3
lead	0.5 µg/m^3	0.5 µg/m^3
nickel	20 ng/m^3	25 ng/m^3

(a) annual mean; limit value for lead, target values for arsenic, cadmium and nickel enter into force 1-1-2013;
(b) see text for further explanation.

Results for the reporting year 2010 can be summarized as follows:

Arsenic: At nearly 90% of the stations a concentration below the lower assessment threshold (2.4 ng/m^3) has been reported. However, at 12 (from the 542 operational stations) the observed concentration is above the reference value and target value set for 2013. A relatively large number of exceedance is observed in Belgium (7 stations of which 4 are located close to one industrial plant in Hoboken, near Anvers (VMM, 2009)). The remaining five exceedances are seen in Czech Republic, Germany, Poland and Slovakia. In two exceedance situations arsenic has been on "aerosol", that is, a not-further defined size fraction.

The majority of stations recorded a slight reduction in arsenic concentrations in the period 2006–2010, although it is worth stressing that the sampling and measurement method was not reported for some stations and the methods might have changed during the period. The short period of the assessment makes it impossible to undertake a statistical analysis of the concentration trend and its statistical significance.

Cadmium: Air concentrations are in excess of the reference value and target value at 10 of the 588 operational stations. Exceedances are observed in three countries (Belgium, Bulgaria, Spain) mainly at industrial, traffic and (sub)urban stations. At the majority of the other stations concentrations are below the lower assessment threshold (2 ng/m^3). Similar to arsenic the majority of stations recorded a reduction in concentrations during the last five years. Concentrations are significantly decreasing at all (14) stations in Switzerland over the last 10 year (2001-2010).

Lead: In 2010 the concentrations of lead were at 99% of the stations below the lower assessment threshold of 0.25 µg/m^3. At two stations (in Bulgaria and in Romania) the reference value and limit value has been exceeded.

Nickel: Exceedances of the target value are seen at 8 of the 551 operational stations; these stations are located in Belgium, Germany, and Italy. Most of the exceedances are related to industry. At 5 stations the reference value has been exceeded.

Although the 4th daughter directive request Member States to perform (indicative) measurement of mercury, at – at least – one background stations, the available data in AirBase is still limited. Background concentrations of mercury in air in 2010 ranged from 1.3 to 2.0 ng/m3 over large parts of Europe (17 stations in Germany, Finland, Lithuania, Poland, Sweden and Slovenia). Aerosol-bound concentrations are orders of magnitude lower (in general less than 0.02 ng/m3) bit a few outliers, up to 6.5 ng/m3, have been reported. Measurements artifacts can not be excluded. Deposition measurements are reported at 20 stations (of which 18 are located in Germany and the United Kingdom). Averaged over all stations the annual flux is 0.10 g/ha/year which is in the same range as the 5th percentile of the critical load for mercury for health- and eco-toxicological effects (Coordination Centre for Effects, CCE Status Report 2010).

3.8.   Population exposure

Table 3.2 gives an overview of the most stringent EU limit or target value set for the protection of human health. The EU value is compared with the AQG recommended by the WHO. A first estimate of the urban population exposed to concentrations above the EU reference value and the AQG is given. This estimate refers to the situation for the period 2006-2010 and it is based on the methodology for the Urban Air Quality indicator CSI004 (EEA, 2011).

When using the EU limit or target values as reference, the highest exposure rates are seen for ozone and PM$_{10}$ and, too a lesser extent, for PM$_{2.5}$ and NO$_2$. When ambient levels are referred to the WHO reference set ozone and both PM size fractions ranks the highest; with a fraction of more than 50% exposed to level above the AQG, SO$_2$ is also of concern. Up to 20% of the urban population is exposed to levels above the reference for NO$_2$, benzene and benzo(a)pyrene. It should be mentioned that due to the smaller number of urban background station the calculation for benzene, B(a)P and lead are less reliable.

In Table 3.2 the exposure of the urban population is compared with exposure estimates as reported[6] by EU27 Member States in the AQ Questionnaire (EC 2004b). In the questionnaire a different approach is used than in the CSI04 indicator. Here not the urban but the total population in the EU Member States is considered. Another difference is that in CSI004 the analysis is based on concentrations averaged over the (sub)urban background stations while the air quality status of an air quality management zone depends on the highest level observed at any of the station located in the zone.

Two discrepancies are found in case of NO$_2$ and B(a)P. Following the reporting procedures in the Questionnaire, a whole air quality management zone is in non-attainment when an exceedance is observed at one single situation. This will frequently be the case for NO$_2$ where many exceedances are observed at many traffic hot–spots. In these situations the whole population in the zone and not the population living in the exceedance area is counted as (potentially) exposed. In case of B(a)P the exceedances are not confined to urban areas but are observed in large regions in Eastern Europe (Figure 3.25).

Table 3.2. Estimate of the fraction of the population resident in EEA32 urban areas potentially exposed to level above the reference level. As reference levels the most stringent EU limit or target levels and the WHO Air Quality Guidelines or deduced reference value (see note b) (average period and concentration, in μg/m^3 unless indicated). The last column gives an exposure estimate as reported[6] under the Air Quality Questionnaire decision (2004/461/EC).

component	EU reference value (a)	Exposure estimate (%)	WHO reference value (b)	Exposure estimate (%)	Exposure according to AQ questionnaire
PM$_{10}$	day (50)	20 - 40	year (20)	80 - 90	17
PM2.5	year (25)	8 – 12	year (10)	90 - 94	14
ozone	8-hour (120)	14 - 50	8-hour (100)	> 95	36
NO$_2$	year (40)	6 - 19	year (40)	6 - 19	50
SO$_2$	day (125)	0 – 3	day (20)	54 - 73	<1
CO	8-hour (10 mg/m^3)	0 – 2	8-hour(10 mg/m^3)	0 – 2	<1
benzene (a)	year (5)	< 1	year (1.7)	13 - 19	1
B(a)P	year (1 ng/m^3)	3 – 8	year (0.12 ng/m^3)	12 – 20	24
lead	year (0.5)	< 1	year (0.5)	< 1	<1

Colour coding of exposure estimates, fraction of urban population exposed to concentrations above the reference level:

	< 10%	10-50%	50-90%	>90%	

a) EU limit or target value, see Table 2.1 for a more complete definition
b) WHO AQG or reference value estimated assuming an additional lifetime risk of 1 x 10^{-5}, see text in paragraph 3.7.

4.   Air pollution and daily life

Air pollution is an (unwanted) result of human activities. Bad air quality may result from natural sources but, in general terms, the anthropogenic emissions give by far the largest contribution to air pollution in Europe. When looking in more detail to the temporal and spatial patterns of air pollution concentrations, the impact of our day-by-day activities on the pollution levels become clear. The concentration maps as shown in this report and by de Smet et al (2010) show a high spatial correlation between population density and pollution levels: large emissions take place generally in areas where people are living and working. In and downwind of large conurbations high pollution levels are often observed. In this chapter we will focus on the temporal patterns. We will give examples how economic but also recreational activities of our society are reflected in the concentration levels.

4.1.   Homo economicus

The daily routine of getting to work in the morning and returning home in the evening is directly reflected in the concentrations of traffic related pollutants. The increasing transport emissions during the morning and evening rush hours lead to a double peak in the diurnal concentration profile (see the examples presented in Figure 4.1). At least, during the working days the rush hours are reflected in the concentrations. On Saturday peaks are less prominent; on Sunday no peak is seen at all. Clearly, in the weekend we sleep late and traffic starts later on the day. At that time the atmosphere
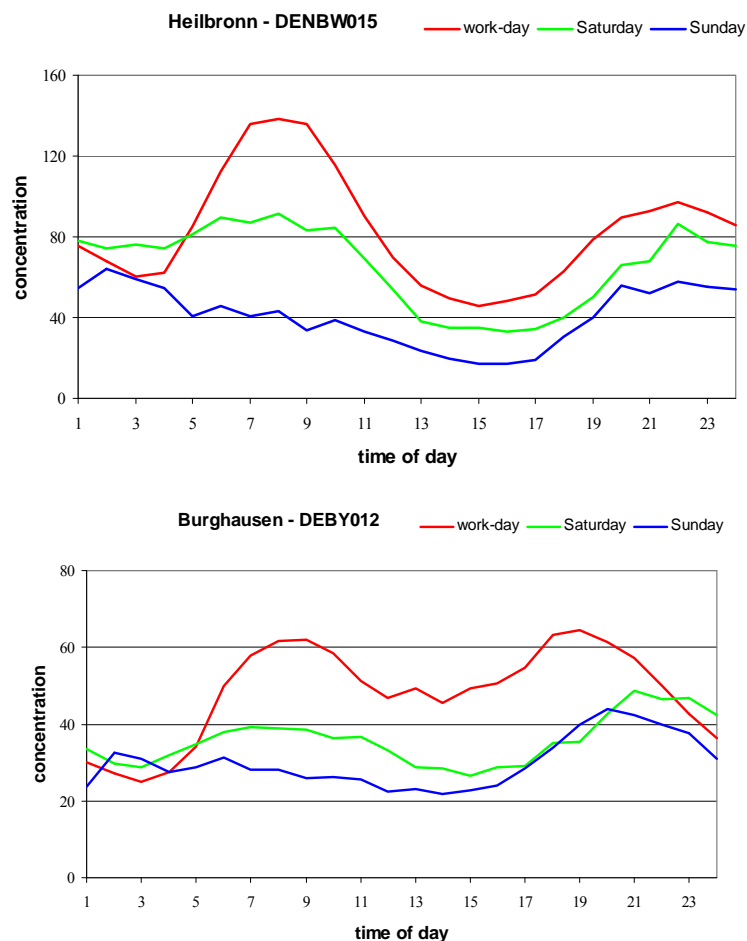
Figure 4.1. Diurnal profiles of NO$_x$ concentrations (as µg NO$_2$/m^3) on working days, Saturday and Sunday at two urban traffic stations.
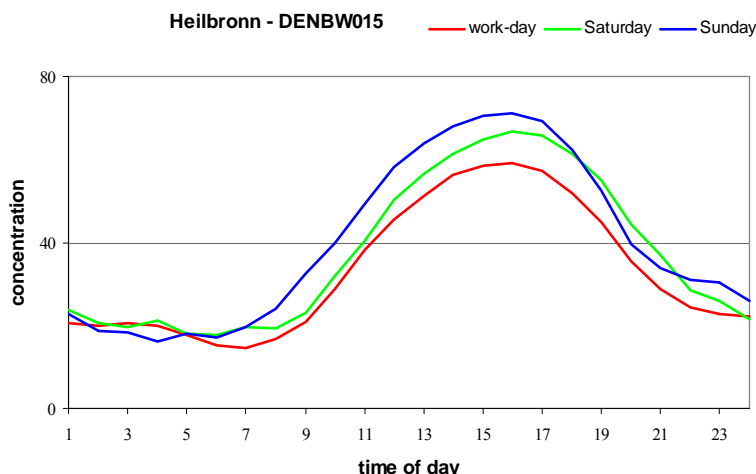
Figure 4.2. Diurnal profile of ozone concentration (µg/m^3) at an urban traffic station during working days, Saturday and Sunday.

is general less stable and this results in lower concentrations. On Sunday the diurnal profile is much smoother than on working days indicating that traffic flows are more constant over the day.

The ozone concentrations show a different behaviour (see Figre 4.2 for the Heilbronn station DENBW015; at the Burghauseen station DEBY012 ozone is not measured). Two main processes (atmospheric stability and photochemical production) determine the profile; the importance of each process will depend on place and time. During the night, early morning ozone concentration tends to decrease due to deposition and quenching by freshly emitted NO_x. In the morning the process of fumigation (Hewson, 1945) starts: due to the incoming solar radiation the night-time inversion is broken and by the increased (vertical) turbulence the relative high ozone levels trapped above the mixing layer are mixed downwards. This, in combination with an increased photochemical ozone production due to an increased irradiation, leads to a peak in the late afternoon. Then, when the sun gets down, photochemistry slows down and the atmosphere becomes more stable again; a new inversion will be formed. Ground level will be decoupled from the layer at higher levels. At the ground level ozone will be removed by deposition or NO_x quenching.

The weekly cycle in traffic intensity is mimicked in the difference in concentrations during the week: concentrations of traffic related pollutants like NO_x, and – to a lesser extent – CO and benzene are lower during the weekend. However, ozone concentrations are higher in the weekend (less NO_x and therefore less chemical quenching of ozone) than on working days (Figure 4.3). This well-known "weekend effect" has been observed since the mid 70s (Cleveland et al, 1974). Satellite measurements (Beirle et al, 2003) have shown that the weekly cycle differs by regions due to differences in cultural and religious traditions. While a Sunday minimum in NO_2 concentrations (Figure 4.3) is seen in the western oriented region (Europe, USA, South Africa), the lowest values are seen in Israel on Saturday (Sabbath). In the Middle East there is a slight weekly effect with lowest concentrations on Friday.

Brussels European Parliament — O3 — NOx — CO — Bnz
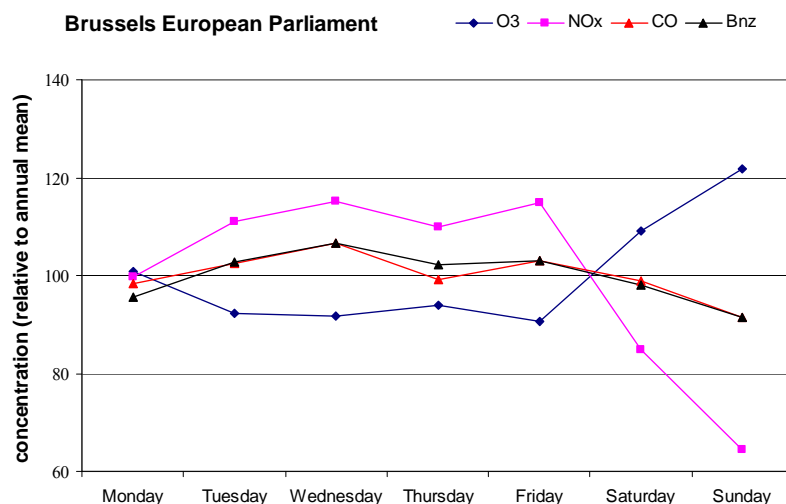
Figure 4.3. Weekly cycle of ozone, NOx, CO and benzene at an urban background station (European Parliament, Brussels). Concentrations are given relative to the annual mean value; data for 2009.

As our daily activities are directly reflected in the ambient concentrations, one might expect that the annual switch from winter- time to summertime could also be observed. On the last Sunday in March we set the clock forward by one hour. Rush hour will start therefore one hour earlier compared to the solar time in an atmosphere which is – on the average- more stable than during the week before the time switch as meteorology (solar radiation, turbulence, etc.) follows solar time. Emissions in a more stable atmosphere will result in higher concentrations and in the days after switching to summer time a slightly higher concentrations are expected. At the end of the summer time period, when switching back to winter time, a similar situation will occur. Although the change to summer time can be seen at individual stations (Figure 4.4), a statistical analysis did not show a significant difference in concentrations of NO_x or O_3 before and after the change. However, at the start of the daylight saving period in spring the averaged NO_x concentration at urban traffic stations increases averaged over the period 2006-2009 with about 8%.

Amsterdam-Florapark — Wintertime — Summertime
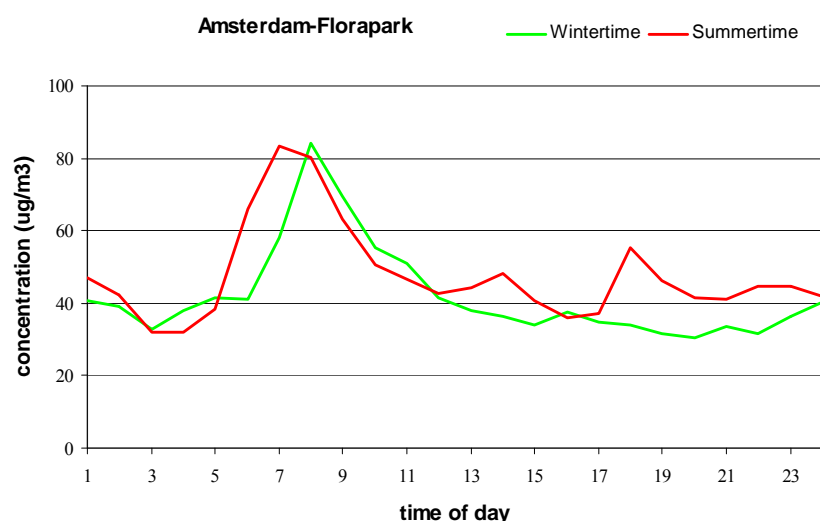
Figure 4.4. Diurnal variation of NO_x concentrations at an urban station in Amsterdam averaged over the 6 days before and the 6 days after the change to summer time on 29 March 2009.

4.2. Homo ludens

Air quality also plays a role in our leisure activities. Its role in painting, see Monet's House of Parliaments (Baker and Thornes, 2006), in poetry and lyrics (see the poem "*Ozone*" published by WS Gilbert in 1865 just 25 years after the discovery of ozone by Schönbein (1840), or the song *Pollution* of Tom Lehrer[9]), in literature (see the description of Coketown in the novel *Hard Times* by Charles Dickens, and the complaints of bad air and dirty laundry in the Dutch city of Schiedam (near to Rotterdam) in the novel *Sara Burgerhart* by Aagje Deken and Betje Wolf[10]) are just a few (historical) examples of the link between arts and air pollution. More – and even older – examples are given by Brimblecombe and Ogden (1977).
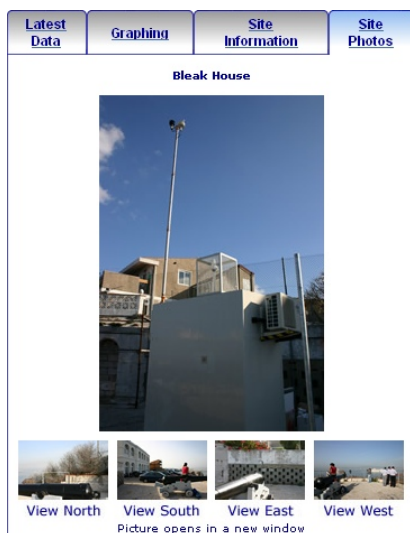
The urban background station Bleak House in Gibraltar.

In his work Charles Dickens has made more references to air pollution; in his book *Bleak House* (1853) he wrote:
'I asked him whether there was a great fire anywhere? For the streets were so full of a dense brown smoke that scarcely anything was to be seen. "Oh dear no, miss", he said, "This is a London particular." '
Bleak House is also the name of a monitoring station in Gibraltar (GB0051A)[11]. It is not clear to us whether this is just a coincident or that there is a link between the two Bleak Houses. Certain is, however, that concentrations in Gibraltar's Bleak House are notably lower than those suggested in Dickens' Bleak House: annual mean concentrations of PM_{10} and NO_2 around 30 and 25 µg/m^3, respectively; ozone concentrations exceed 120 µg/m^3 on 7-20 days.

In March 2011 a leading anti-pollution campaign group in Hong Kong was using art as a new weapon in the fight for clean air in this metropolis[12]. Enlisting the support of 40 artists and the auction house Sotheby's, the Clean Air Network organized an auction of 51 environment-inspired works of modern art in – as they say it - the first awareness and fund raising event of this kind. The artworks include sculptures, paintings and photographs. But all artworks illustrate environmental issues and problems, like smog, waste, climate change and the destruction of natural habitats.

This T-shirt, protesting against the bad air quality, was sold during the Olympic Games in Los Angeles, 1984.

In current times, air pollution has become a topic of discussion in the organisation of mega events like the Olympic Games. During the games in Los Angeles in 1984, action groups demonstrated against the high smog level. For the 2008 Olympic Games in Beijing numerous measures were taken – successfully - to improve the air quality during the games (see e.g. UNEP, 2011; Xing et al, 2011; Wang et al, 2009). However, Mother Nature deserves a gold medal for cleaning the air: rain at the beginning and wind during the Games likely contributed about half of the effort needed to clean up the skies (Gao et al,

---

[9] On his album "That was the year that was", 1965. see: http://www.youtube.com/watch?v=JPrAuF2f_oI
[10] http://www.letterkundigmuseum.nl/tabid/92/BiographyID/28/BiographyName/BetjeWolffenAagjeDeken/Mode/BiographyDetails/Default.aspx
[11] http://www.gibraltarairquality.gi/stats.php?t_action=data&t=1&site_id=GIB2&map=&g=7&s=&dy=
[12] http://www.nytimes.com/2011/03/22/business/global/22pollute.html?_r=3

2011). Similar measures were taken to improve the air quality during the Shanghai World Expo (CAI, 2011) and the Commonwealth Games in Delhi in 2010[13].The 2012 Olympic Games in London are supposed to become the greenest games ever[14].

Looking at the distances which we travel during our holidays, it will be evident that tourism, or recreation in general, is an important source of air pollution. In Flanders half of the trips are for recreational purposes (30%) or for shopping (20%). On the average a Flemish person travels daily about 40 km; of this 13 km (31%) is for recreation and 5 km (9%) is for shopping (Komino, 2010). For the Netherlands it is estimated that in 2005 more than 60 billion holiday-kilometres were travelled (Mulder et al, 2007). This is about 4000 km per person per year. In other European countries similar numbers can be expected. Altogether, this recreational travelling leads to substantial emissions. On the other hand, it should be mentioned here that the travel-related emissions of professionals working in the field of climate change or air quality are also substantial (Stohl, 2008).

Recreational travelling is not only by car or airplane; there are about 6 million recreational boats in the EU. In summer the NO_x emissions from these boats can be significant around big lakes and popular seashores. The European Commission has proposed stricter limits for NO_x, hydrocarbons and PM for recreational boats (EC, 2011).

During national or cultural holidays a "holiday effect", similar to the weekend-effect, has been noted outside Europe with concentrations significantly different between holidays and non-holidays. In Israel the Day of Atonement (Yom Kippur) is an official holiday. During this day all motorized transportation and most of the industrial activities cease for a 24 h period. The NO_x concentrations during the Day of Atonement are significantly lower than the days before or after demonstrating the impact of the strong reduction of local emissions. Concentrations of particulate matter are very similar during the Day of Atonement and the days before and after; direct, local emissions of PM are small and the contribution of long-range transport is in this case more important (Dayan et al, 2011).

During the Chinese New Year (CNY) family reunions is an important tradition an example of which is in the Taipei metropolitan area where a substantial fraction of the residents travel back to their hometowns just before the CNY period and return directly after the New Year period (Tan et al, 2009). During the CNY period a significant reduction of traffic is observed. The concentrations of NO_x, CO, VOC, SO_2 and PM_{10} are lower in the CNY period than in the non-CNY period while ozone shows an opposite behaviour which is mainly due to the NO titration (Tan et al, 2009).

In Europe we are not aware of events during which a similar large reduction in traffic might be expected. The World Carfree Day (22 September) would be an opportunity to study the impact of traffic emissions. Although more than 2100 European cities and towns in 34 countries participated in the European Mobility week[15], only in a limited number of then organised an *»In Town Without My Car!«* event, i.e. setting aside one or several areas that are reserved solely for pedestrians, cyclists and public transport for at least one whole day (i.e. 1 hour before to 1 hour after normal working hours). When traffic is stopped at street or neighbourhood level, the effect on concentrations will be small and hardly detectable because of meteorological variations.

A unique situation like the Chinese New Year with a large temporal reduction in urban population in a metropolitan area during a well-defined short period is unknown in Europe. The summer holiday period is in most countries spread over a period of 8-10 weeks. The perception of most people is that this result in a reduction in the "normal' rush hour traffic jams but significant observable changes in concentrations are not to be expected.

---

[13] http://megaevents.cleanairinitiative.org/node/746.
[14] http://www.london2012.com/sustainability
[15] see http://www.mobilityweek.eu/-Participating-cities-.html for a list of participating cities and the planned activities.

The period between Christmas and New Year is similar to the CNY period when economy is running at a low level. In a preliminary analysis we used the AirBase data over the period 2000-2009 to see whether the lower economic activities are detectable in the air quality data. For the period 18 December – 8 January the number of exceedances of a daily NO_2 concentration of 50 µg/m^3 were counted on a daily basis. The exceedances, expressed as fraction of the number of operational stations, were grouped into a pre-Christmas period (18 -24 December), a Christmas period (25 December – 1 January) and a post-Christmas period (2-8 January). Results are summarized in Figure 4.5. Except for Christmas 2007 the lowest number of exceedances is observed during the Christmas period. The highest number of exceedance are found in the pre-Christmas period; a possible explanation is that for many people the Christmas holidays extends to the first week of January, i.e. what we have defined here as post-Christmas period. A similar exercise using the PM_{10} data did not show systematic differences between the three periods. Reasons for this might be the contribution of long-range transport and – more important in this case- the fact that we create a lot of PM emissions during the Christmas period (see below). Note that fixed dates are used here; a year-specific definition of the Christmas holiday period might improve the results.
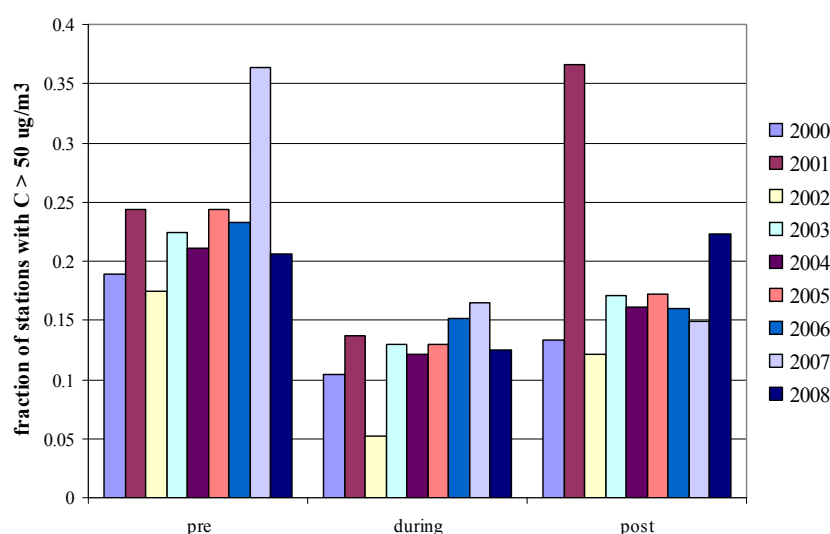
Figure 4.5. Fraction of NO_2 stations where the daily concentration exceeds 50 µg/m^3 during the week before Christmas (pre, 18-24 December), during the Christmas period (during, 25 December – 1 January) and the week after Christmas (post, 2 – 8 January); period 2000-2008.

Concentrations of particulate matter and its composition is a sensitive tracer of our (daily) habits. Even the use of illicit drugs is reflected in particulate matter. The concentrations in PM of drugs like cocaine or heroin show also a clear weekend effect: concentrations peak during the weekend (Viana et al, 2010; 2011). During the White Nights festival the concentrations of recreational drugs peaked in downtown Rome while in a nearby semi rural location no increases are measured (Cecinato et al, 2009).

At many occasions, during many festivals or celebrations we like to make large fires (Eastern Bonfire, New Year's Eve) mostly in combination with fireworks. In urban areas high PM levels are observed during the turn of the year, see the examples given in Figure 4.6. The magnitude of the firework peak depends strongly on the meteorological conditions. Windy and rainy conditions favours a fast dispersion of the firework emissions while under foggy conditions concentrations may reach extremely high values. The maximum concentrations measured on January 1, averaged over urban and rural station in the Netherlands are shown in Figure 4.7[16]. At urban station the peak is observed at 1:00 AM, at the rural stations the maximum value is reached somewhat later (1:00 – 5:00 AM). The

---

[16] data extracted from http://www.rivm.nl/In_de_Bibliotheek?kwobject=rivmp:4590&contenttype=issue

two peak years (2004/05) and 2007/08) are characterised by dry weather and low wind speeds (< 3 m/s).

PM10

SO2

NO2

NOx
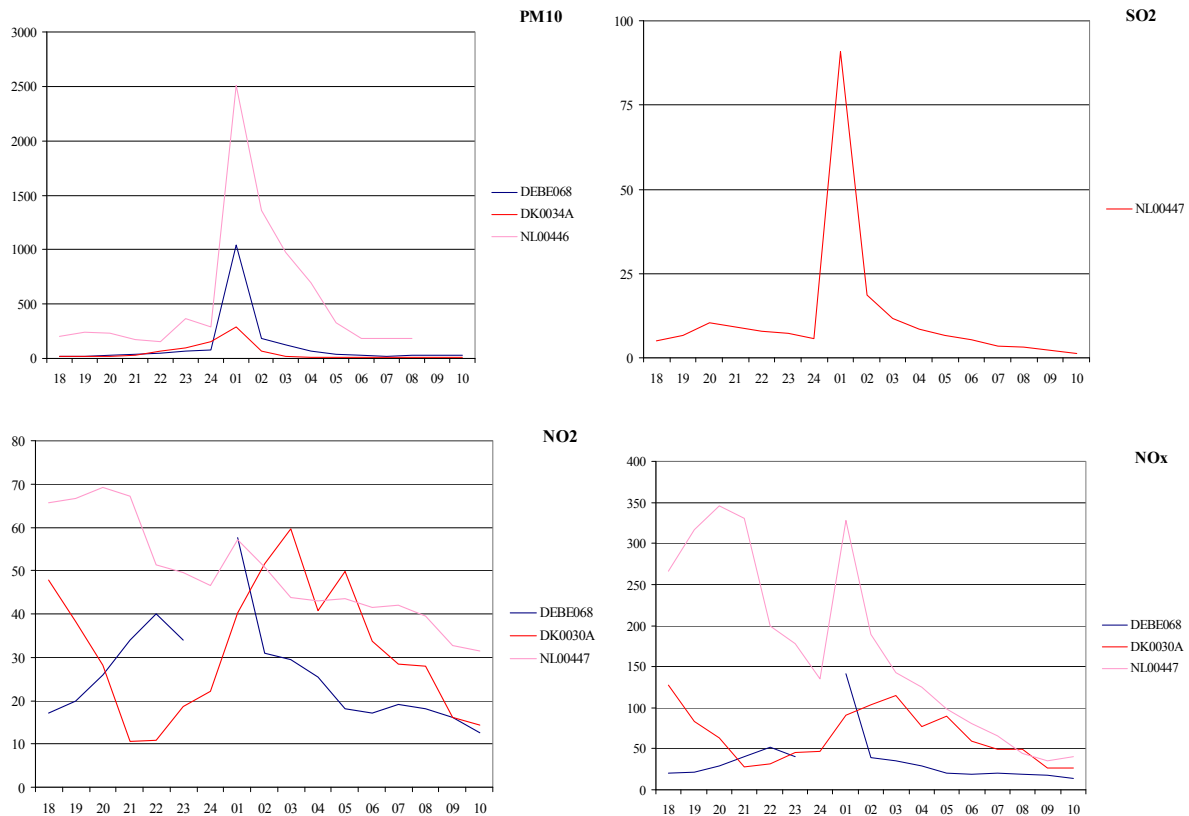
Figure 4.6. Hourly PM$_{10}$, SO$_2$, NO$_x$ and NO$_2$ concentrations (clockwise, starting upper left; concentrations are given in µg/m^3) during new years eve 2007; period 31-12-2007 18:00 – 1-1-2008 10:00.
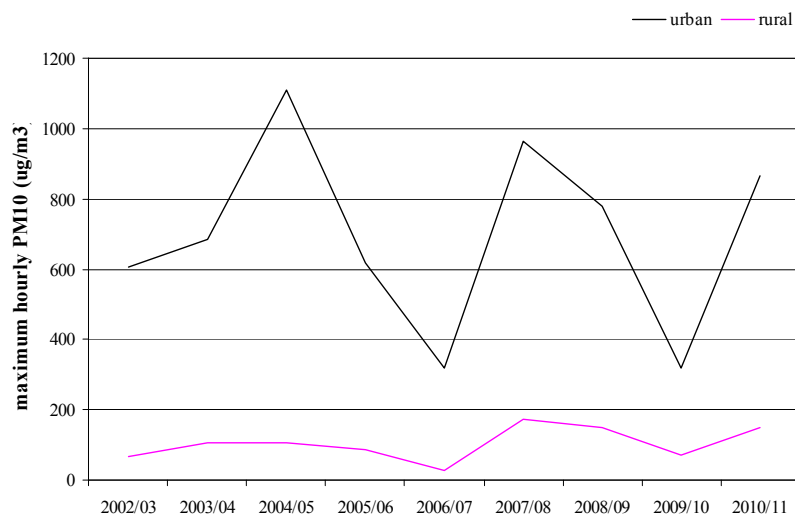
Figure 4.7 Highest PM$_{10}$ concentration (hourly value) averaged over urban and rural stations in the Netherlands.

In addition to the wide-spread firework displays during New Year's Eve, many cities organise their own displays during the year. AirBase data might be used to evaluate these local events. As an example we present here data from Valencia (Spain) during the *Fallas*, a traditional celebration in praise of Saint Joseph from 15-19 March. Throughout *Fallas* fireworks are widely used. It starts already early in the morning with some firecrackers as a "wake-up call". At 14:00 during *La*

Mascaletà smoke-producing firework and firecrackers are ignited. The intensity of *La Mascaletà* increases notably during the festival. At night there are more displays; again each night is progressively grander and the last, 19 March, is called *la nit de foc* , the night of fire. Figure 4.8 shows the PM_{10} and $PM_{2.5}$ concentration measured during the 2010 festival. The PM_{10} and $PM_{2.5}$ concentrations are highly correlated (R^2= 0.95) with an averaged $PM_{2.5}/PM_{10}$ ratio of 0.77. In the early morning of 20 March, at the final stage of the festival *La Cremà*, when also bonfires are lit, concentrations reach a maximum. At the end of the festival, the contribution of the fine fraction, likely related to combustion aerosol, increases to 85-90% of total PM_{10}. During the 2005 *Fallas* similar patterns have been observed although concentrations were lower (Morenso et al, 2007).

Bonfire and fireworks during La Cremà, the last event of the Valencia festival (photo: Laura Aalbers).

The composition of firework-related aerosol contains high concentration of metals like potassium, aluminium, magnesium, lead, barium, strontium, copper, antimony, persistent organic and inorganic toxics like PAH and perchlorate (Shi et al, 2011; Joly et al, 2010;Morenso et al, 2007; Nishanth et al, 2012). Elemental and organic carbon are major contributors as well (Vecchi et al, 2008).

During firework displays the urban population could be exposed to extremely high concentrations. The exposure period is relative short (several hours) but the WHO (2006) Air Quality Guidelines set for daily mean PM concentrations will be easily exceeded on these days. The impact of firework-related air pollution on human health is still unclear. The observed PM concentrations are within or above the concentration intervals used in a number of human exposure studies as reviewed by the WHO (2006). Although the results of these exposure studies are not fully consistent, the concurrent occurrence of high levels of fine particles and other toxic substances suggest that adverse health effects are to be expected due the exposure to firework-related air pollution. The concentrations reported to AirBase have been measured at urban background or traffic stations; most likely these stations are located at some distance of the places where the firework is lit. The spectators and the (professional or amateur) pyro-technicians will be exposed to higher levels.

Another of the more unusual recreational activities that may lead to substantial emission are bonfires. A bonfire is a controlled outdoor fire as part of a celebration. Celebratory bonfires are typically designed to burn quickly and may be very large. Many of the bonfires have a traditional origin and are held annually. In Great Britain bonfires are lit on Guy Fawkes Night to mark the failure of the Gunpowder Plot of 5 November 1605 in which a number of Catholic conspirators attempted to
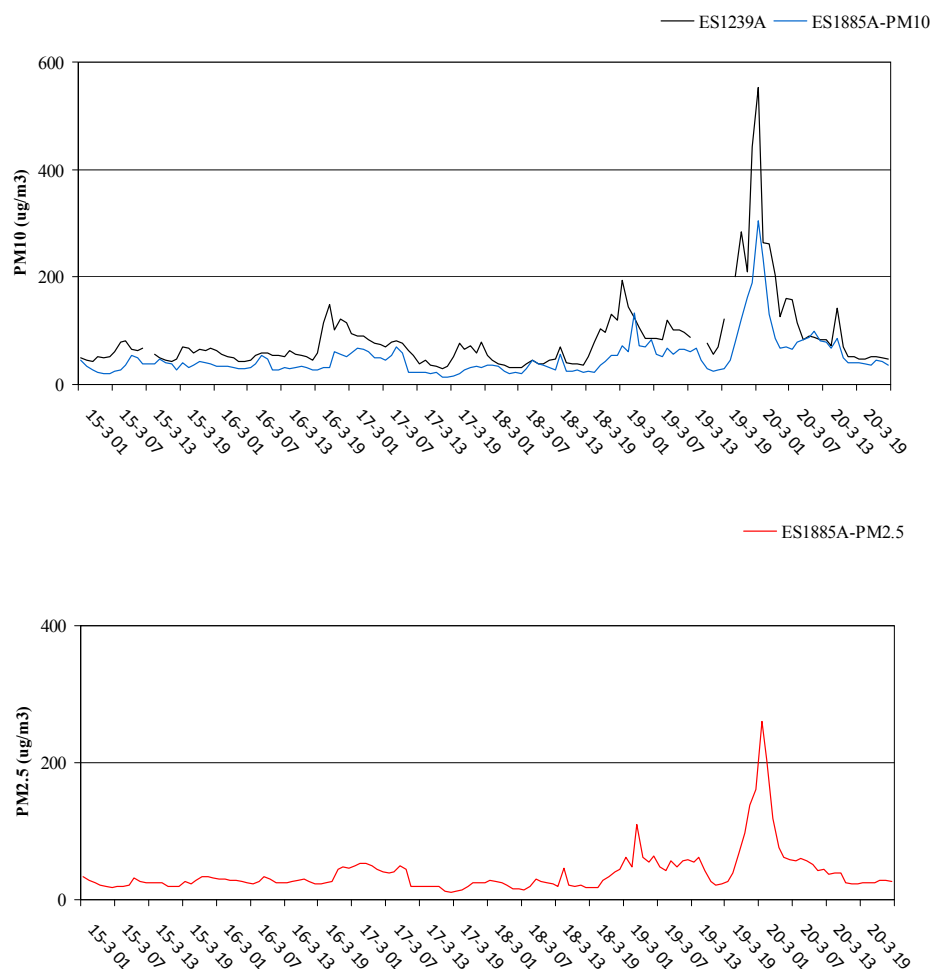
Figure 4.8. Hourly PM$_{10}$ (top) and PM$_{2.5}$ (bottom) concentrations measured at two stations in Valencia during the Falals festival, March 2010.

destroy the House of Parliaments in London. Although 5 November is the official date, nowadays the fires might be lit on days just before or after the 5th. Figure 4.9 shows the hourly PM$_{10}$ and PM$_{2.5}$ concentrations at some station in the UK on 5 and 6 November 2009. In the late afternoon, early evening (18:00 – 20:00) of 5 November concentrations sharply increased. More than 80% of total PM10 is in the fine fraction (PM$_{2.5}$). Similar high particulate levels are observed in the beginning of November 2007 (AEA, 2007). Peaks are spread out over the period 4-6 November depending on the region.

The Easter Bonfires are very popular in the eastern and north-eastern parts of the Netherlands and in the neighbouring German regions. During the Easter weekend in 2006 (15 and 16 April), on Saturday evening around 22:00 concentrations started to increase sharply in northern Netherlands. During the night concentrations of more than 200 µg/m^3 were observed at urban stations in the cities of Groningen (N Netherlands) Bremen and Hamburg (NW Germany). Concentrations remain high during the night. In course of Sunday morning the pollution is transported in an eastern direction. At that time, wind speed increased and it started to rain and concentrations dropped to normal levels again in the late afternoon (Figure 4.10). It can be concluded that Guy Fawkins Nights and the Eastern Bonfires may cause a significant air quality problem under certain (stable, low-wind) conditions.
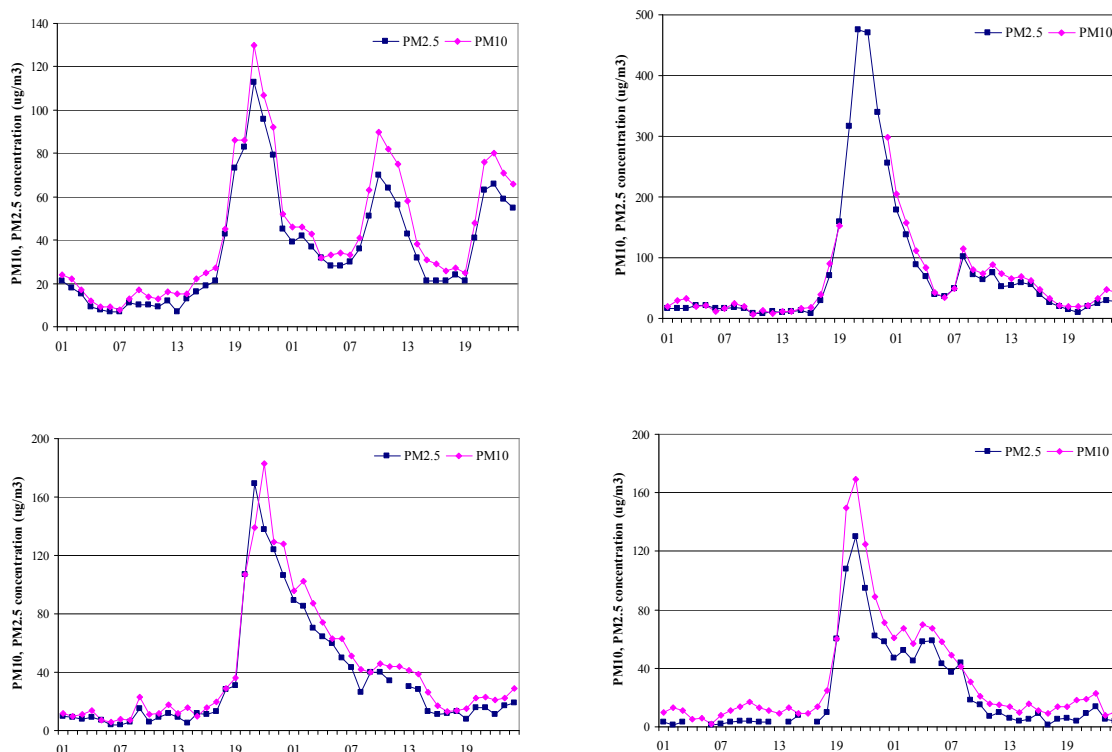
Figure 4.9. PM$_{2.5}$ and PM$_{10}$ concentrations at the urban background stations (clockwise, starting upper left) GB0584A, Leeds Centre; GB0776A, Hull Freetown; GB0776A, Liverpool Speke and GB0615A, Sheffield Centre on 5 and 6 November 2009.
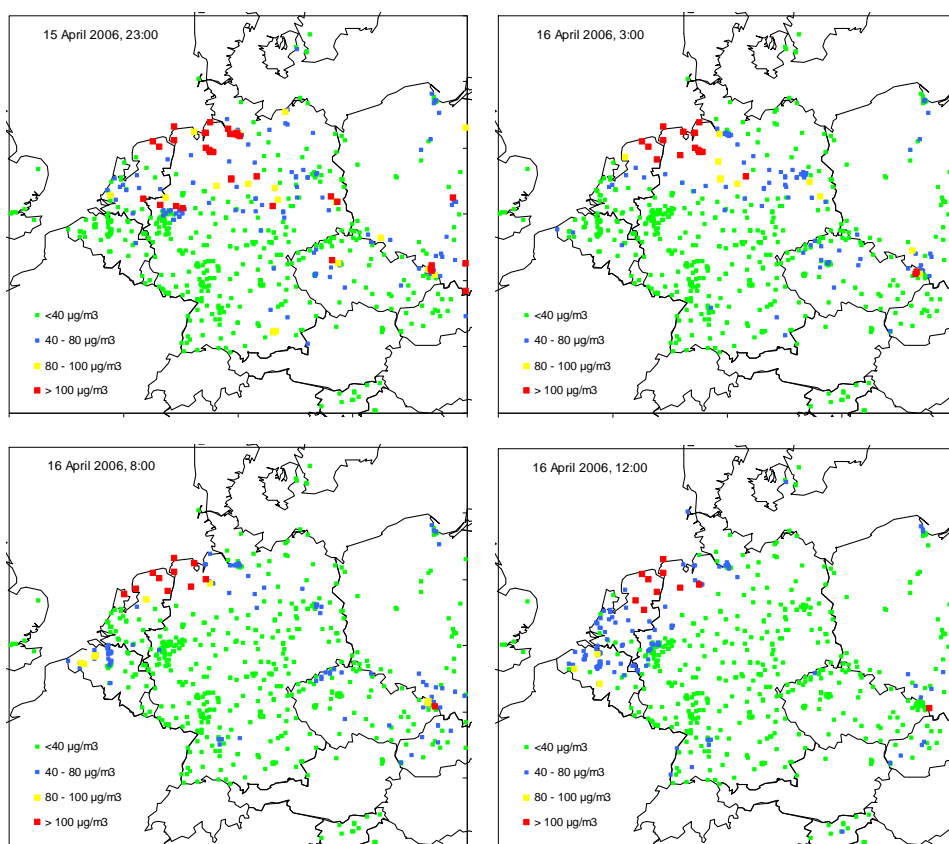
Figure 4.10. High PM$_{10}$ concentrations have been observed in the North-eastern Netherlands and bordering regions in Germany during the Eastern weekend in 2006.

5. OZONE PRECURSORS

In this chapter a review of the measurements of Volatile Organic Compounds (VOC) will be given. Next to NO_x, CO and methane (CH_4), VOC are ozone precursors. Monitoring of these pollutants is required since 2003 by the third daughter directive on ozone (EC 2002) and later included in the Air Quality Directive (EC 2008: AQD).

5.1. Requirements in Air Quality Directive

According to Annex X in the Directive 2008/50/EC on ambient air quality and cleaner air for Europe (EC 2008) Member States have to assess concentrations of ozone precursor substances.
The main objectives of such measurements are to detect any trend in ozone precursors, to evaluate the efficiency of emission reduction strategies, to check the consistency of emission inventories and to help attribute emission sources to observed pollution concentrations. An additional aim is to support the understanding of ozone formation and precursor dispersion processes, as well as the application of photochemical models. Additionally the measured levels of VOC ozone precursors may provide valuable information for the investigations of the origin of secondary organic aerosol (SOA).
A list of volatile organic compounds recommended for measurements is given in Table 5.1.
Following the Directive, measurements shall be taken in particular in urban or suburban areas at any monitoring site set up in accordance with the requirements of the Directive and considered appropriate with regard to the monitoring objectives given in the Annex X to the Directive. A reference method to measure the precursors is not defined; Member States shall inform the Commission of their methods used to sample and measure the precursors.
The Member States report on meta information in relation to VOC-measurements and of the observed concentrations under the Exchange of Information decision, a summary of the data is also reported by the Air Quality Questionnaire (EC, 2004).

Review of the VOC-list
The role of an individual VOC in photochemical ozone formation depends on its reactivity and on the time scale considered. For the long-term exposure to ozone VOC-reactivity is less important; low reactive but abundant species like CO and CH_4 are important for the build up of the hemispheric background concentrations. For understanding ozone formation the monitoring of NMVOC, CO, CH_4 NO_x and in background air will be needed. To follow changes in precursor emissions, monitoring closer to (specific) sources, for example, in urban areas, should be considered.
When considering short-term peak ozone concentrations (summer smog) the reactivity of the individual VOC is of importance. The VOC-list (Table 5.1) has been compared with two different VOC reactivity scales: the POCP-concept (Photochemical Ozone Creation Potential) developed by Derwent et al (1998) and the MIR-scale (Maximum Incremental Reactivity) developed by Carter (1994). Table 1 gives the POCP- (Derwent et al., 2007) and MIR-values (Carter, 1994) for the VOC listed in the AQ Directive. Although the ranking within both scales differs, there is a good correspondence in the most (and least) reactive species.

Reviewing the AQ Directive-list with the POCP-values given by Derwent et al. (2007), a few reactive VOC with a POCP-value of 100-105, are missing, namely, *cis*- and *trans* 2-hexene, 1,2,3,5 tetramethylbenzene, 1,2,4,5, tetramethylbenzene, 3,5 dimethylethylbenzene and methyl-glyoxal. Compared to Carter (1994) all highly reactive VOC with a MIR-value of 8 or higher are included with the exception of methyl glyoxal.

However, next to the reactivity the ambient level determines the relative contribution of an individual VOC to ozone formation. Concentrations of 2-hexenes are estimated to be two to five times lower (Schürmann et al, 2007; Lai et al, 2004) than the concentrations of the 2-pentenes which

Table 5.1. List of VOC ozone precursors as recommended in Annex X of the AQ Directive (a). Reactivity and relative ranking of VOC as listed in the AQ Directive. POCP values taken from Derwent et al. (2007), MIR-values taken from Carter (1994); mean, maximum and minimum annual mean concentration ($\mu g/m^3$) and number of stations as reported[6] under the air quality questionnaire (EC, 2004), reference year 2010.

component	POCP	rank	MIR	rank	mean	max	min	# stations
Ethane	8	29	0.25	30	3.47	9.00	0.87	19
Ethylene	100	10	7.4	12	1.64	4.70	0.08	17
Acetylene	7	30	0.5	27	0.49	1.05	0.04	16
Propane	14	27	0.48	28	3.47	22.00	0.70	19
Propene	117	1	9.4	5	1.17	9.20	0.16	17
n-Butane	31	25	1.02	22	1.70	21.00	0.14	47
i-Butane	28	26	1.21	20	1.08	6.70	0.08	29
1-Butene	104	9	8.9	7	0.38	2.29	0.04	40
Trans-2-Butene	116	2	10	3	0.11	1.20	0.00	41
cis-2-Butene	113	4	10	4	0.12	1.40	0.03	39
1,3-butadiene	89	12	10.9	1	0.16	1.90	0.01	34
n-Pentane	40	19	1.04	21	0.84	4.20	0.13	56
i-Pentane	34	22	1.38	19	0.96	9.60	0.09	45
1-Pentene	95	11	6.2	15	0.21	1.90	0.01	40
2-Pentenes (b)	110	5	8.8	9	0.11	0.50	0.02	32
isoprene	114	3	9.1	6	0.21	2.00	0.03	50
n-Hexane	40	20	0.98	23	1.98	45.20	0.01	56
i-Hexane (2-methylpentane)	41	18	1.5	18	0.34	0.82	0.07	32
n-heptane	35	21	0.81	25	1.11	25.70	0.03	55
n-octane	34	23	0.6	26	0.19	1.30	0.02	46
i-octane(2-methylheptane)	34	24	0.96	24	1.25	16.50	0.01	38
benzene	10	28	0.42	29	1.37	6.70	0.01	579
toluene	44	17	2.7	16	3.25	26.10	0.00	400
Ethyl benzene	46	15	2.7	17	0.92	17.11	0.06	241
m,p-xylene	79	13	7.4	11	1.49	15.40	0.00	270
o-xylene	78	14	6.5	14	0.78	10.51	0.00	257
1,2,4-Trimethylebenzene	110	6	8.8	10	0.59	8.39	0.00	54
1,2,3-Trimethylebenzene	105	8	8.9	8	0.26	0.90	0.04	21
1,3,5-Trimethylebenzene	107	7	10.1	2	0.16	1.60	0.01	42
formaldehyde	46	16	7.2	13	3.24	9.10	1.90	8
Total non-methane hydrocarbons	-	-	-	-	204	1400	0.20	21

(a) in the draft Guidance on the Commission implementing decision on a reporting on ambient air quality, the (preferred) IUPAC names are given in addition to the trivial names;

(b) in AQ Directive and in the draft guideline 2-pentene is listed. Most likely this refers to the sum of the two isomers *cis* and *trans* 2-pentene (the two isomers have similar POCP- and MIR-values (POCP-values are 109 and 111, MIR-values are 10.0 and 10.0 for the *cis*- and *trans*-isomer, respectively). Optional a separate listing (like for *cis*- and *trans*-2-butene) could be considered).

have a similar reactivity on the POCP scale. The tetramethylbenzenes are known to be emitted by passenger cars (Caplain et al, 2006). Ambient concentrations are relatively low, about 10-30% of the concentrations of the equally reactive trimethybenzenes and about 1-10% of the concentration of the slightly less reactive xylenes (Pankow et al, 2003). Methyl-glyoxal is a product formed during the degradation of isoprene and aromatic hydrocarbons (Monks et al, 2009; Zhang et al, 2011). Methyl-glyoxal is mainly in the particulate phase; gas phase concentrations are about 20 ng/m^3 on a total (particulate + gaseous) ambient concentration of 120 ng/m^3 (Ortiz et al, 2006). In view of their low ambient concentrations the contribution of these VOC to the ozone formation will be small; there is no reason to include them in the recommended list in the AQ Directive.

Within the EMEP programme (ECE/EB.AIR/GE.1/2009/15: monitoring strategy 2010-2019) the list of VOC required to be measured at the level 2[17] sites is in agreement with the requirements of the AQ Directive. At level 3 sites (monitoring at these sites is mainly research-driven) it is recommended to monitor a number of VOC according to the WMO GAW report No 172. The GAW-report recommends to measure various oxygenated hydrocarbons (e.g. methanol, ethanol, acetone). The contribution of these oxidation products to episodic ozone formation will be small and monitoring at sub-urban locations will not be necessarily. To improve our understanding of relevant atmospheric-chemical processes it could be recommended to measure these pollutants at rural background stations in coordination with EMEP , for example at the same background locations as mentioned in Art6.5 of the Directive related to PM measurements.

Reporting of VOC
Member States report on VOC measurements by means of the AQQ at an aggregated level and by means of the Exchange of Information Decision at a more detailed level (hourly and/or daily concentrations) (EC 1997). Some inconsistencies between the two data flows and within the various reporting forms in the AQ Questionnaire are noted. Stricter quality control on the reported data needs to be considered.

The number of stations where VOC are measured differs widely, per Member State and per individual VOC. All Member States report on one or more of the recommended VOC; Spain is the only country where the full list of recommended VOC is measured. The aromatic C_6-C_8 hydrocarbons (benzene, toluene, xylenes, ethyl benzene) are measured in nearly all Member States; in a number of MS monitoring is limited to these aromatic VOC. Of the 31 recommended VOC benzene is the only pollutant for which monitoring is mandatory in order to assess the air quality in relation to the limit value set in the AQ Directive. The other VOC, in particular the C_2-C_3- VOC, are measured at a substantially lower number of stations. Formaldehyde is measured in two Member States only. Annual mean concentrations for 2010 as reported in the questionnaire are given in Table 1. The reported concentrations may differ by several orders of magnitude.

Information on the type of stations is not directly given in the questionnaire. By combining the meta-information in AirBase with the information in the questionnaire, Table 5.2 is prepared. 39 stations listed in the Questionnaire could not be traced in AirBase. Monitoring is done at all type of stations (Table 5.2). In line with the requirements of the Directive each Member State operates at least one station in an (sub)urban environment.

Table 5.2. Classification of VOC monitoring stations, situation 2010.

type of area	type of station			
	Background	Industrial	Traffic	Total
rural	55	16	1	72
suburban	75	60	17	152
urban	133	36	181	350
Total	263	112	199	574

5.2. Trends in ozone precursors

Monitoring and reporting on the VOC relevant for ozone formation should have been started in 2004, at least on one station per Member State. Evaluating the available data in AirBase showed that

---

[17] In the EMEP network three kind of monitoring sites are defined: level 1 sites provide long-term basic chemical and physical measurements; level 2 sites provide additional physical/chemical speciation of relevant components; activities at level 3 sites are research-oriented aiming at improving the scientific understanding of relevant processes in relation to air pollution and its control.

for the period 2004-2010 the consistent set of stations[18] is very small. For the C_2-C_4 VOC, two stations, the urban background station Eltham (London) and the traffic station Marylebone Road (London), fulfil the criteria.

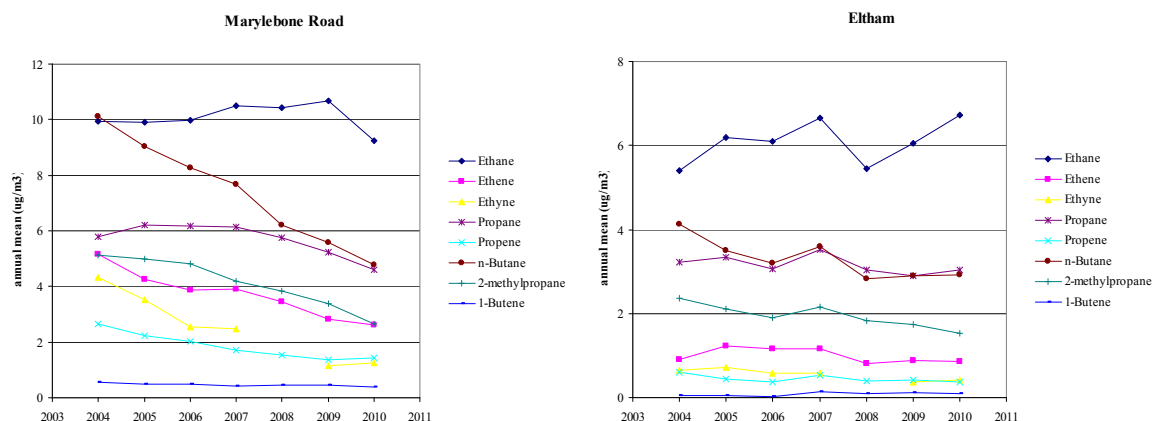*Figure5.1. Annual mean concentrations of VOC at an urban background and traffic station in London, period 2004-2010.*

The concentrations of C_2-C_4 VOC (including *cis-* and *trans*-2-butene, not shown in Figure 5.1) at the traffic site are higher that those in the urban background. Road traffic is an important source of VOC. With exception of ethane, the other VOC have a clear downward trend at the traffic location. At the urban site a significant downward trend is not seen; on the other hand, although we might tentatively conclude that concentrations are not increasing.

The UK has set objective for 1,3-butadiene a running annual mean concentration of 2.25 µg/m^3 to be met by 31 December 2003**.** Time series are available for five stations; with levels of less than 0.6 µg/m^3 exceedance of the objective has not been observed in the period 2004-2010. Concentrations tend to decrease at traffic and urban locations; no change is seen at the rural station Harwell. For the C_5-C_7 hydrocarbons a similar pattern is seen: long time series are only available for the two London stations, with a downward trend at the traffic location and no significant trend at the urban location. n-Heptane is also measured at a rural station in the Netherlands; no trend is observed here.

Time series of benzene have been discussed in Chapter 3. Time series of toluene are available at 63 stations, mainly at traffic locations. At three out of every four traffic stations there is a significant downward trend. At the 12 urban and 4 rural stations a downward trend is seen at 9 and 3 stations, respectively. The other aromatics are measured since 2004 at 1 to 11 stations. Similar to the other VOC, decreasing concentrations are observed at traffic locations and no trend at the other station types.

In conclusion we can state that although monitoring of the VOC ozone precursors was recommended already in the first ozone directive (92/72/EEC) and mandatory since 2004, the available data in AirBase is very limited. Most data is available for benzene and toluene; significant downward trends are seen for both pollutants in various Member States. For the other VOC long time series have been reported for two stations in London; at the traffic location most of the VOC show a significant downward trend, at the urban site trends are in general not significant.

---

[18] For the VOC selection criteria are: annual data coverage of more than 50%, operational during 6 or 7 years in the period 2004-2010.

6. ARE WE MISSING DATA?

6.1 Introduction

In the 2008/50/EC directive on ambient air quality and cleaner air for Europe (AQD; EC 2008) data quality objectives for air quality assessments have been set. In this way a certain harmonisation of the assessment procedures within the Member States is realised. Depending on the assessment method (fixed measurements, indicative measurements, modelling or objective estimation) different objectives are set for uncertainty and, in case of measurements, on data capture and time coverage. Which of the four assessment methods might be used, depends on the actual air quality levels in relation to the limit or target values.

In this section we will focus on the uncertainties in measurements due to incomplete time coverage. The uncertainties set as data quality objective in the Directive are given for individual measurements averaged over the period considered by the limit (or target) value for a 95% confidence interval. Next to the uncertainty associated with a single measurement, missing data in time series will introduce additional uncertainty. The uncertainty will depend on the data coverage, that is, the fraction of the year for which valid measurements are available. The AQD acknowledges that a lower data coverage is acceptable when "random measurements" are used. A clear definition of random sampling is not given in the Directive but is described in various examples:

- distributed over the year to be representative of various conditions for meteorology and traffic (for fixed measurements of benzene);
- one day's measurement a week at random, evenly distributed over the year, or eight weeks evenly distributed over the year (indicative measurements);
- evenly distributed over the year in order to avoid skewing of results (fixed and indicative measurement of pollutants included in the fourth daughter directive (EC, 2004a).

Procedures to test these requirements are not given.

In this chapter we will develop simple, pragmatic procedures for testing whether measurement data is randomly distributed over the year. With an increase in the missing data, the uncertainties in air quality indicators, in particular those defined as a limited number of exceedances per year, will increase. In the second part we will evaluate what the minimum data coverage should be in order to avoid an unacceptable increase in uncertainty due to incomplete time series.

6.2 Defining "random sampling"

Air pollutant concentrations show a large temporal variability at different time scales. This variability is caused by the meteorological variability leading to differences in dispersion or dilution and the variability in emissions of primary pollutants caused by human activities. These processes lead to a distinct diurnal profile strongly related to the diurnal profile of meteorological parameters although at monitoring stations close to emissions sources the daily variation in human activities might be reflected.

In view of this variability a test on how random a set of data is, should therefore be applied at different timescales. Based on the phenomenology of air pollutant concentrations we will consider here:

1. the diurnal variation: the hourly concentration data should be randomly distributed over the 24 hours in a day;
2. the weekly variation: during the weekend days concentrations tend to be, depending on the pollutant and/or location, systematically higher or lower than during working days. The requirement here is that the daily concentration data is randomly distributed over the seven days in a week;

3. for most pollutants there is an annual variation: the daily concentration data should be randomly distributed over the 12 months in a year.

The testing of an evenly distribution of the hourly values over the day, days of the week or months can be compared with the rolling of a dice with 24, 7 or 12 sides. For the distribution over the hours in a day we expect that for each hour there are μ_0 data points with

$$\mu_0 = dNp$$

where N is the number of hours per year (N = 8760), d is the data coverage and p is the probability for one specific hour in a day(p = 1/ 24).
The standard deviation is given by:

$$\sigma^2 = dNp\left(1-p\right)$$

If the actual observed number of hourly values is given by x_i the relative deviation from the expected value μ_0 is given by:

$$z_i = abs\left[\left(x-\mu_0\right)/\ \sigma\right]$$

A large z_i value implies that for that specific hour the number measurement is (much) lower than expected.
A similar approach has been followed for the distribution of valid daily data over the weekdays and over the months. Note that if a daily mean is calculated from hourly values at least 75% of the hourly averages (i.e 18 hourly values) are required.

Results

The random test has been applied to the hourly data available in AirBase for the main components (SO_2, PM_{10}, O_3, NO_2 and CO) for 2009. For fixed measurements the AQ Directive requires a data coverage of 90% but this does not include losses of data due to the regular calibration of the normal maintenance of the instrumentation. Assuming that these tasks require about 5% of the time, the requirements of the Directive corresponds with an effective data coverage of 85% (Garber et al, 2001). For the gaseous pollutants 83-95% of the stations has a data coverage of 85% or more; of the station reporting hourly PM_{10} value, 80% fulfil this requirement.

An overview obtained after screening the time series with a data coverage of 85% or more but having a $z_{max, daily}$ of less than 3 is given in Table 6.1. Assuming a normal distribution, a $z_{max, daily}$ of more than 3 corresponds to the exceptionally unlikely situation that the number of observation is outside the range of $\mu_0 \pm 3\sigma$. A closer look at the distribution over the day shows that there are frequently none or very few measurements for one specific hour. For the gaseous pollutants SO_2, NO_2, CO and O_3, 12-19% of the stations do not meet the DQO; adding the requirement of a random distribution during the day increase the loss in stations to 22-36%. Missing one specific hour will result in a systematic error in daily values and all other aggregated parameters. Although the data coverage fulfils the requirements of the Directive, the use of these stations in assessments is disputable. A plausible explanation is that in some networks the monitors are calibrated every 24 h. *By changing the interval to 23 or 25 hours the systematic error now expected at 10% to 20% of the stations measuring SO_2, NO_2, CO and O_3 will be reduced*.

For daily measurements a similar screening, now focussing on a random distribution during the week and during the year is made. The results (Table 6.2) show that for the gaseous pollutants CO and ozone there is a marginal difference between the number of stations proving hourly and daily data. These pollutants are exclusively measured automatically. For NO_2 and SO_2 there are about 140-170 additional stations measuring on a daily bias; this concerns manual measurements. However, when comparing the total number of stations and the number having a data coverage of 85% or more, it is clear that the majority of the manual stations does not fulfil the DQO. A large increase in the number of stations is seen for PM10 (+ 1853 stations). But again we must note that the increase in the

number of stations having a 85% data coverage is less (+ 1297) leading to the conclusion that the DQO are not fulfilled at a large fraction of the manual stations.

When screening the daily time series on a random distribution over the week, it is seen that no measurements of SO_2, NO_2 and PM_{10} no measurements are performed during one or both weekend days at 40-70 stations. For stations fulfilling the DQO the requirement of random distribution is not a problem. With two days systematically missing, the data coverage drops below the DQO of the Directive and generally also below the 75%-criteria as usually applied by the ETC (see e.g. Mol et al, 2011). For data coverages of 75% or more, an uneven distribution of data over the weekdays will not form a problem. However, when lower data coverage criteria are accepted (e.g. down to 40%, see the discussion below) the use of these station may lead to biased results. For the automatic measurement (ozone, CO) testing on a random distribution over the week does not result in a further rejection of stations.

When also a random distribution of data over the year is required, 16% (ozone) to almost 30% (PM_{10}) of the stations has to be rejected. The requirement of a random distribution over the year has a relatively large impact on the number of stations; data losses occur apparently during a (large) number of consecutive days.

The uncertainties in European-wide assessments will depend on the quality of the data and of the spatial coverage of the stations used in the assessment. As discussed above the temporal representativeness of selected time series can be improved by adding criteria on random sampling but this will exclude a number of stations (Table 6.1 and 6.2). The price of this might be a worsening in the spatial coverage. The optimal mix of spatial coverage and data quality will depend on the type of assessment (pollutant, choice of air quality indicator). Below, criteria on data coverage in relation to the selected indicator will be discussed.

Table 6.1. Total number of stations reporting hourly values, number of stations having a data coverage of more than 85, 75 or 60% and number of stations having also a $z_{max, daily}$ of less than 3, reference period 2009.

pollutant	total number	Coverage > 85%	Cov > 85% and $z_{max, daily} < 3$	Coverage >75%	Cov > 75% and $z_{max, daily} < 3$	Coverage >60%	Cov > 60% and $z_{max, daily} < 3$
SO_2	2031	1657	1306	1794	1401	1876	1461
NO_2	3093	2614	2185	2820	2340	2913	2415
O_3	2241	1979	1748	2089	1839	2136	1876
CO	1352	1091	895	1186	969	1231	1004
PM_{10}	1319	1061	1054	1136	1127	1187	1177

Table 6.2 Total number of stations reporting daily values, number of stations having a data coverage of more than 85, 75 or 60% and number of stations having also a $z_{max, weekly}$ and/or $z_{max, monthly}$ of less than 3, reference period 2009.

pollutant	total number	Coverage > 85%	Cov > 85% and $z_{max, weekly} < 3$	Cov > 85% and $z_{max, weekly} < 3$ and $z_{max, monthly} < 3$	Coverage >75%	Cov > 75% and $z_{max, weekly} < 3$	Cov > 75% and $z_{max, weekly} < 3$ and $z_{max, monthly} < 3$	Coverage >60%	Cov >60% and $z_{max, weekly} < 3$	Cov > 60% and $z_{max, weekly} < 3$ and $z_{max, monthly} < 3$
SO_2	2178	1734	1734	1634	1875	1874	1679	1974	1961	1693
NO_2	3267	2680	2680	2533	2913	2911	2609	3017	3003	2611
O_3	2246	1988	1988	1884	2089	2089	1911	2139	2139	1912
CO	1355	1085	1085	1031	1176	1176	1056	1232	1232	1058
PM_{10}	3172	2358	2354	2228	2581	2572	2300	2766	2744	2316

6.3 Requirements on data coverage

In checking of the compliance of the air quality levels with the legally binding threshold value, the DQO as given in the AQ Directive have to be fulfilled. By this a number of stations will be excluded and which might lead to a loss in information in particular in areas with a less dense network. By lowering the criterion on data coverage more stations will be included in the assessment but uncertainties will increase. For certain type of assessments small increases in uncertainties might be acceptable in view of further assumptions made in the assessment. What an acceptable coverage is, will depend on the (temporal behaviour of the) pollutant and on the requested indicator: the maximum hourly value will be more sensitive to missing values than the annual mean concentration.

To investigate this we have tested this sensitivity for the set of indicators related to the limit or target values as listed in the AQ Directive using a monte-carlo approach.

Firstly, for hourly data time series with a 100% coverage were selected (or created from nearly complete time series where missing values were imputed using a simple interpolation). Time series for different pollutants, different station type having different diurnal and annual behaviour have been selected (see Table 6.3). By randomly excluding observations, new time series having a data coverage in the range 40-90% were created. The random selection procedure has been repeated 1000 times; for each indicator mean and standard deviation is calculated. Using the definition of randomness given above, the generated time series are random having an averaged $z_{max, hourly}$ of 1.25 (0.73 – 1.77; 95% confidence range); $z_{max,weekly}$ and $z_{max, monthly}$ are both less than 0.25.

Table 6.3. Characteristics of stations used in the monte-carlo simulations. Note that gap-filled time series, not the actual measured series have been used in the simulations.

Eol_code	station name	lat	lon	altitude	type of station	type of area
BG0026A	Galabovo	42.15	25.91	136	Background	urban
DENI071	Barbis-Verkehr	51.61	10.42	273	Traffic	suburban
DESH034	Pinneberg Damm	53.66	9.81	7	Traffic	urban
ES1480A	ES1480A-IJ-BARCELONA (GRACIA-SANT GERVASI)	41.40	2.15	75	Traffic	urban
FR01016	Atton	48.89	6.09	203	Industrial	rural
FR08209	Gard Rhodanien2	43.94	4.68	85	Industrial	rural
FR39010	Rocade Concorde	14.61	-61.05	80	Traffic	urban
IT0503A	BZ1 Via Amba Alagi 402104	46.50	11.34	266	Background	urban
IT1698A	CORSO EUROPA/VIA SAN MARTINO - GENOVA 701068	44.41	8.97	75	Traffic	urban
IT1851A	GA1 Gargazzone 2102126	46.58	11.20	290	Background	suburban
NO0015A	Rådhuset	60.39	5.33	5	Background	urban
PT02004	Estarreja/Teixugueira	40.68	-8.58	20	Industrial	suburban
PT06004	São João	32.65	-16.91	46	Traffic	urban
SK0020A	Zilina - Obezná	49.21	18.77	356	Background	urban

As missing values tend to cluster, a second set of monte-carlo simulations has been made in which it was assumed that if data for one specific hour is missing, the probability that also the data for the next hour is missing, is 97%. The results are still "random" although the $z_{max,weekly}$ and $z_{max, monthly}$ values are substantially larger: 0.64 (0.18-1.10) and 1.65 (0.77-2.53), respectively. In the discussion below this selection will be indicated as pseudo-*random.*

Evaluation of the sensitivity for missing values is based on the environmental objectives given in Table 6.4. The limit or target vales as set in the 2008/50/EC and 2004/107/EC Directives and are either based on an annual mean value of on a maximum number of exceedances of hourly or daily values of a certain threshold level. When *N* exceedances are allowed, the limit or target value is met when the *(N+1)th* highest value is below the threshold. Alternatively, compliance is also met when the percentile value corresponding to the allowed number is below the threshold.

Table 6.4. Summary of limit or target values (averaging period and allowed number of exceedances) and corresponding statistical indicators

Pollutant(s)	Averaging period for LV/TV	Max number of exceedances	Indicator-1	Indicator-2
SO_2, NO_2, PM, 4th DD-pollutants	annual mean	-	annual mean	-
SO_2	day	3	4th highest value	99.18 percentile
	hour	24	25th highest value	99.73 percentile
NO_2	hour	18	19th highest value	99.79 percentile
PM_{10}	day	35	36th highest value	90.41 percentile
O_3	day	25	26^{ht} highest value	93.15 percentile

The results for the hourly based target values of SO_2 and NO_2 are presented in Figure 6.1, both for the pure random selection as for the pseudo-random selection. Not shown are the results for the annual mean values. In the case of pure random losses the difference in annual mean between the 100%-coverage and coverages as low as 40% lies within a range of ± 10% (2 σ). Two stations are selected here: the Bulgarian station shows the largest deviation from the reference level whereas the French station shows a pattern more representative for the selected stations. The conclusions for these cases are clear: the indicator based on the *(N+1)th* highest value results in an increasing underestimation of the reference value. When using the percentile-based indicator an underestimation up to 5 % is seen. In the pseudo-random case the underestimation is similar, however, the uncertainty increases.
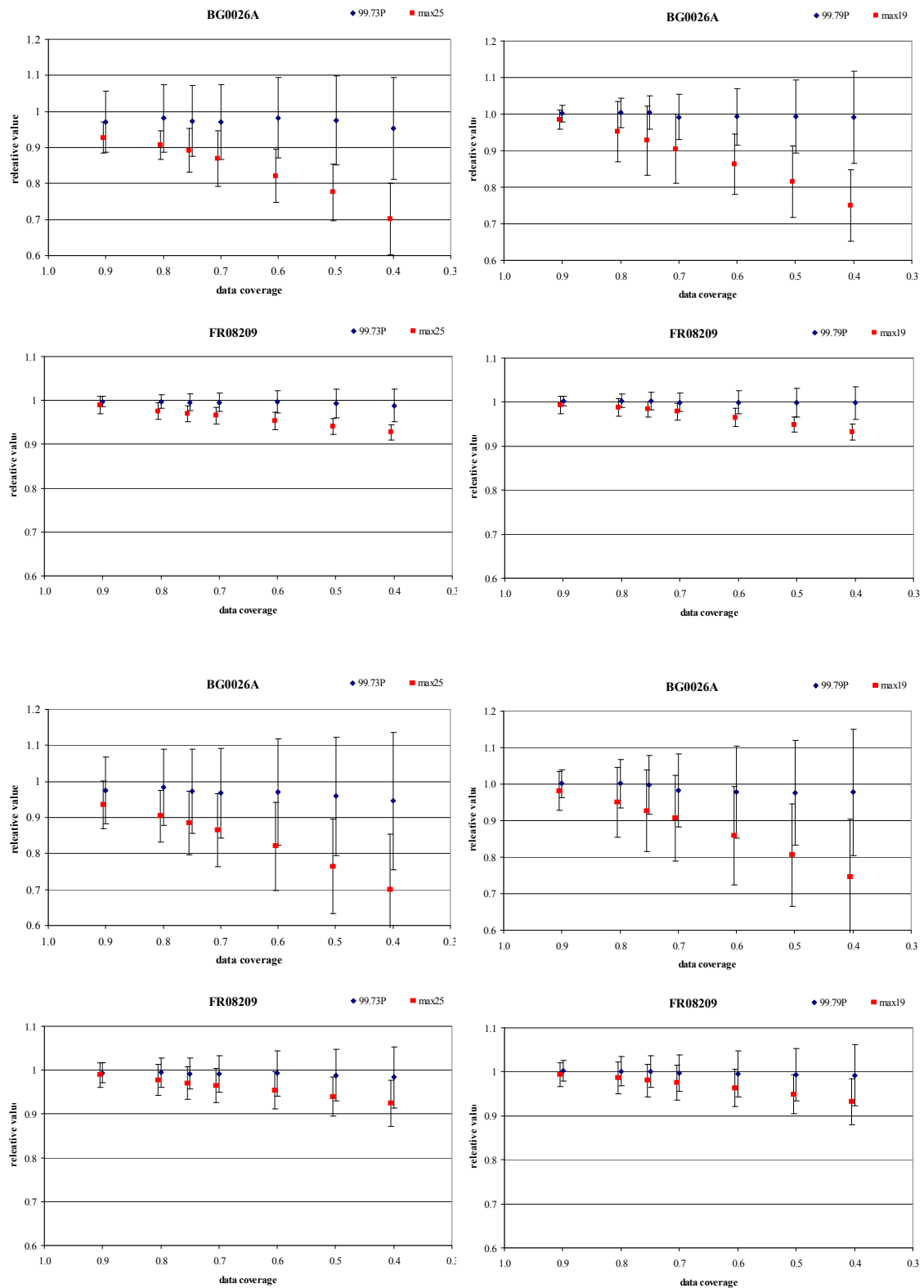
Figure 6.1. Relative values of the 25th highest value and the 99.73-percentile (left) and the 19th highest value and the 99.79-percentile (right) as function of the data coverage. The errors bars correspond to the 95% confidence level (2 σ). Top panel is given for a pure random simulation; bottom panel is for the pseudo-random simulation.

These conclusions also hold for the skewed concentration distribution found for the rural industrial station FR01016. The annual mean concentration at this station is low but the peak values (19th and 25th highest hourly value) are extremely high (40-45 times the mean value), see Figure 6.2. Depending on the wind direction the station is hit by the plume of a nearby located industrial complex. By a data coverage of 40% the 99.73- and 99.79-percentiles are underestimated by 2-3% but uncertainties are high (standard deviation of about 20% for the random simulation; 40% in the pseudo-random simulation). The 19th and 25th highest values are strongly underestimated by about 40%.
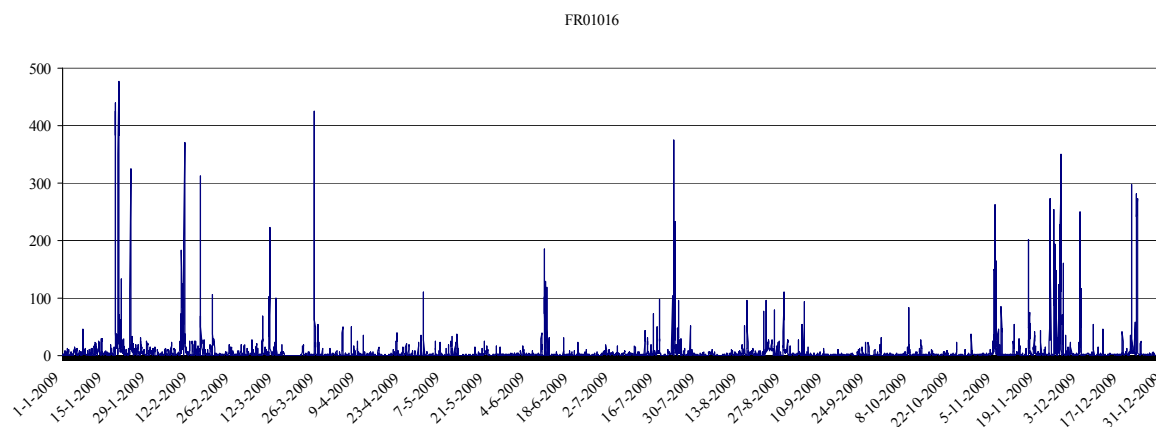
FR01016

Figure 6.2. Time series (reference period 2009) for the rural industrial station FR01016 as used in the monte-carlo simulations.

Similar monte-carlo simulations are made for daily values. Using random sampling the annual mean concentration does note deviates more than 1% of the reference value, even with a data coverage of 14% (the minimum data coverage for indicative measurements as required by the AQ Directive). The uncertainty introduced by the random sampling increases with lower data coverage. For data coverages of 30% or more, an uncertainty of ± 10% (median values for the 12 time series used in the simulation) is found. Such an additional uncertainty compared with continuous measurements is judge to be acceptable for compliance checking (Working Group on benzene, 1997). At a data coverage of 14% the additional uncertainty is about 15-17%.
A notable exception is formed by the data for station FR01016. At this station an exceptionally high ratio between maximum daily mean and annual mean of more than 20 is observed; at the other stations this ratio is 3 or less. At this station a standard deviation of 0.34 and 0.54 is found for a data coverage of 30 and 14%, respectively.
Conclusion: for annual mean values the additional uncertainty introduced by incomplete time coverage is less than 10% (at the 95% confidence level) for data coverage of 30% or more.

Similar as in case of the hourly limit values the *(N+1)[th]* highest value and the corresponding percentile value (Table 6.4) have been compared for the daily limit or target values. Results (Figure 6.3) are comparable to the results obtained in the hourly exercise: the percentile based indicator performs well, even for a data coverage of 14%, the difference with the reference value is less than 8%. However, the introduced uncertainty exceeds 10% for data coverages of 50% or less. The *(N+1)[th]* highest value increases with decreasing coverage. A systematic underestimation of 8%, averaged over the 12 stations, is seen already at a data coverage of 75%.

Conclusions
A simple tool for testing how randomly missing values are distributed over a time series has been proposed. Applying this test showed that at a number of automatic stations hourly data for one specific hour is systematically missing. A plausible explanation is that in some networks the automatic monitors are calibrated every 24 hours at a fixed moment. By changing the calibration
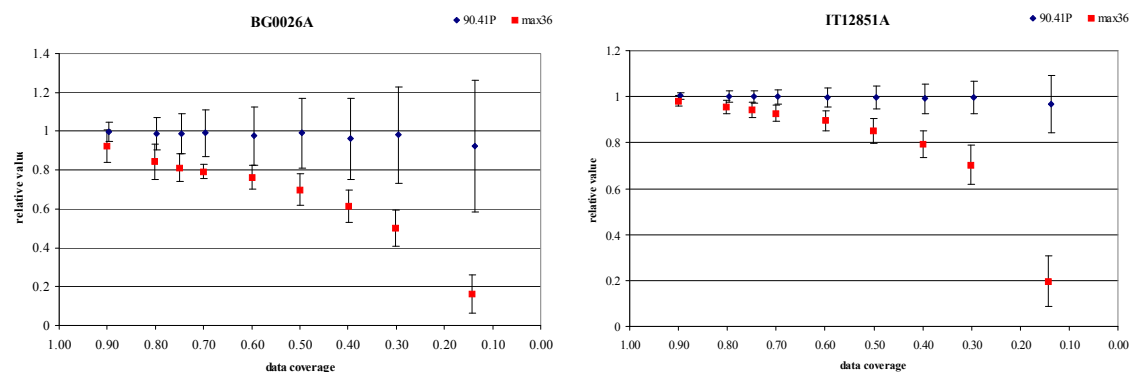
Figure 6.3. Relative values of the 36ᵗʰ highest daily value and the 90.41-percentile (left) as function of the data coverage. The errors bars correspond to the 95% confidence level (2 σ).

interval from 24 to 23 or 25 hours the systematic error now expected at 10% to 20% of the stations measuring SO_2, NO_2, CO and O_3 will be reduced.

For manual measurements it is noted that at a number of stations data for specific days in the week (generally at Friday or during the weekend) is missing. This results in systematic errors which could be avoided by a different sampling procedure.

The test further flags stations where during at least one calendar month the data coverage is less than about 25%. Generally such stations are included in assessment as long as the annual data coverage is 75% or more. However, when data is missing during long, consecutive periods the aggregated values might show an unknown bias. Excluding these stations will reduce the overall uncertainty in the assessment.

By means of monte-carlo simulations it has been shown that – as long as missing values are randomly distributed over the year – at a data coverage of 30% an additional uncertainty of 10% is introduced due to incomplete time-coverage. However, in assessments based on annual means it should be borne in mind that by selecting only stations having a random data loss the reduced uncertainty might be out-balanced by the better spatial representativeness when less stringent criteria are applied. For example, in 2009 there are 470 stations reporting daily benzene data and having a data coverage of 75% or more. Of these 295 stations fulfil the requirements for random data losses. Relaxing the requirement of data coverage to 30%, there are 324 stations fulfilling the requirements for random data losses.

When assessments are referring to the hourly or daily limit or target values, an indicator based on the (N+1)ᵗʰ highest value should be avoided. This indicator increasingly underestimated the 'true' value with decreasing data coverage. When using the corresponding percentile value no bias is observed for data coverages of 50% or more. The additional uncertainty due to incomplete time coverage is less than an acceptable 10%.

ACKNOWLEDGEMENT

REFERENCES

AEA (2007) Air Pollution Forecasting report: Bonfire Night 2007. AEAGroup, Didcot, UK.

Baker J, Thornes JE (2006) Solar position within Monet's Houses of Parliament. Proc Roy Soc A 462, 3775-3788

Barrett K., Fiala J., de Leeuw F., Ward J. (2008) Air pollution by benzene, carbon monoxide, PAH's and heavy metals. ETC/ACC Technical Paper 2008/12. See also: http://air-climate.eionet.europa.eu/reports/ETCACC_TP_2008_12_AQstatus_Benz_HM_CO_PAH

Beirle S, Platt U, Wenig M, Wagner T (2003) Weekly cycle of NO2 by GOME measurements: a signature of anthropogenic sources. Atmos. Chem. Phys. 3, 2225-2232.

Brimblecombe P, Ogden C (1977) Air pollution in art and literature. Weather 32, 285-291.

Buijsman E., Beck J.P., Bree L. van, Cassee F.R., Koelemeijer R.B.A., Matthijsen J., Thomas R., Wieringa K. (2005). Particulate Matter: a closer look. MNP report no. 500037011, Bilthoven, the Netherlands. http://www.mnp.nl/bibliotheek/rapporten/500037011.pdf (Dutch version: Fijn stof nader bekeken. MNP report 500037008, http://www.mnp.nl/bibliotheek/rapporten/500037008.pdf)

CAI(2011) Blue skies at Shanghai EXPO -2010 and Beyond. Post-Expo workshop report. Clean Air Initiative for Asian Cities. http://cleanairinitiative.org/portal/projects/ShanghaiExpoBeyond

Caplain I, Cazier F, Nouali H, Mercier A, Déchaux JC, Nollet V, Joumard R, André JM, Vidon R (2006) Emissions of unregulated pollutants from European gasoline and diesel passenger cars. Atmospheric Envirionment 40, 5954-5966.

Carter WL (1994) Development of ozone reactivity scales for volatile organic compounds. J Air Waste Management 44, 881-899.

Cecinato A, Balducci C, Nervegna G, Tagliacozzo G, Allegrini I (2009) Ambient air qia;ity and drug aftermaths of the Notte Bianca (White Night) holidays in Rome. J Environ Monit 11, 200-204.

Cleveland WS, Graedel TE, Kleiner B, Warner JL (1974) Sunday and workdays variations in photochemical air pollutants in New Jersey and New York. Science 186, 1037-1038.

Dayan U, Erel Y, Shpund J, Kordova L, Wanger A, Schauer (2011) The impact of local sources and meteorological factors on nitrogen oxide and particulate matter concentrations: a case study of the Day of Atonement inIsrael. Atmospheric Environment 45, 3325 – 3332.

Derwent, R.G., Jenkin, M.E., Saunders, S.M., Pilling, M.J., 1998. Photochemical ozone creation potentials for organic compounds in Northwest Europe calculated with a master chemical mechanism. Atmospheric Environment 32, 2429–2441.

Derwent RG, Jenkin ME, Pasant NR, Pilling MJ (2007) Reactivity-based strategies for photochemical ozone control in Europe. Environmental Science and Policy 10, 445-453.

de Smet P, Horálek J, Coňková M, Kurfürst P, de Leeuw F, Denby B (2010) European air quality maps of ozone and PM10 for 2008 and their uncertainty analysis
ETC/ACC Technical Paper 2010/10

Draxler, R.R., Rolph, G.D. (2012) HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, Silver Spring, MD.

EC (1997) Council Decision 97/101/EC establishing a reciprocal exchange of information and data from network and individual stations measuring ambient air pollution within the Member States (amended by Commission Decision 2001/752/EC).

EC (2002) Directive 2002/3/EC of the European Parliament and of the Council of 12 Februari 2002 relating to ozone in ambient air. Official Journal L 67, 09/03/2002, pp 14-30.

EC(2004a) Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, Official Journal L23, 26/01/2005, pp 3-16.

EC (2004b) Commission Decision 2004/461/EC laying down an AQ questionnaire to be used for annual reporting on ambient air quality assessment under Council Directives 96/62/EC and 1999/30/EC and under Directives 2000/69/EC and 2002/3/EC of the European Parliament and of the Council.

EC (2008) Directive 2008/50/EC of the European Parliament and of the Council on ambient air quality and cleaner air for Europe. Official Journal L 152(11.6.2008): 1-44.

EC (2011) Recreational boats to become safer and less polluting. Memo/11/542.

Gao Y, Liu X, Zhao C, Zhang M (2011) Emission controls versus meteorological conditions in determining aerosol concentrations in Beijing during the 2008 Olympic Games. Atmos. Chem. Phys., 11, 12437–12451.

Garber W, Colosio J, Grittner S, Larssen S, Rasse D, Schneider J, Houssiau M. (2001): Guidance on the Annexes to Decision 97/101/EC on Exchange of Information as revised by Decision 2002/752/EC. European Commission, DG Environment, Brussels.

Hewson Ew (1945) The meteorological contol of atmospheric pollution by heavy industry. Quart J.R. meteor. Soc. 71, 266-282.

Jimmink B, de Leeuw F, Ostatnicka J, Schreiberova M (2012) Reporting on ambient sir quality aseessment in the EU Member States, 2010. ETC/ACM Technical Paper, in preparation.

Joly A, Smargiassi A, Kosatsky T, Fournier M, Dabek-Zlotorzynska E, Celo V, Mathieu D, Sevranckx R, D'amours R, Malo A, Brook J (2010) Characterisation of particular exposure during fireworks displays. Atmospheric Environment 44, 4325-4329.

Komino (2010) Recreatief verkeer in Vlaanderen. Komino, Gent; Bond Beter Leefmilieu Vlaanderen, Brussel

Lai CH, Chen KS, Ho YT, Chou MS (2004) Characteristics of $C_2^-C_{15}$ hydrocarbons in the air of urban Kaohsiung, Taiwan. Atmospheric Environment 38, 1997-2011.

Mol WJA, van Hooydonk PR, de Leeuw FAAM (2010) European exchange of monitoring information and the state of the air quality in 2008. ETC/ACC Technical paper 2010/1.

Mol WJA, van Hooydonk PR (2012) The European exchange of information in 2011. ETC/ACM Technical paper 2012/1.

Monks PS et al (2009) Atmospheric composition change – global and regional air quality. Atmospheric Environment 43, 5268-5350.

Moreno T, Querol X, Alastuey A, Cruz Minguillon M, Pey J, Rodriguez S, Vicente Miro J, Felis C, Gibbons W (2007) Recreational atmospheric polution episodes: inhalable metalliferous particles from firework displays. Atmospheric Environment 41, 913-922.

Mulder S, Schalekamp A, Sikkel D, Zengerink E, van den Horst T, van Velzen J (2007) Vakantiekilometers en hun milieu-effecten zullen spectaculair blijven stijgen. TNS NIPO, Amsterdam.

Nishanth T, Praseed KM, Rathnakaran K, Satheesh Kumar MK, Ravi Krishna R, Valsaraj KT (2012) Atmospheric pollution in a semi-urban coastal region in India following festival seasons. Atmospheric Environment 47, 295-306.

Ortiz R, Hagino H, Sekiguchi K, Wang Q, Sakamoto K (2006) Ambient air measurements of six bifunctional carbonyls in a suburban area. Atmospheric Research 82, 709-718.

Pankow JF, Luo W, Bender DA, Isabelle LM, Hollingsworth JS, Chen C, Asher WE, Zogorski JS (2003) Concentrations and co-occurrence correlations of 88 volatile organic compounds (VOCs) in the ambient air of 13 semi-rural to urban locations in the United States. Atmospheric Environment 37, 5023-5046.

RIVM (2003) Nuchter omgaan met risico's RIVM report 251701047. RIVM, Bilthoven, the Netherlands.

Rolph, G.D. (2012) Real-time Environmental Applications and Display sYstem (READY) Website (http://ready.arl.noaa.gov). NOAA Air Resources Laboratory, Silver Spring, MD.

Schönbein CF (1840) Beobachtungen über den bei der Elektrolysation des Wassers und dem Ausströmen der gewöhnlichen Elektrizität aus Spitzen sich entwickelden Geruch. Liebigs Amm Chem 50, 616-635.

Schürmann G., Schäfer K, Jahn C, Hoffman H, Bauerfeind M, Fleuti E, Rappenglück B (2007) The impact of NOx, CO and VOC emissions on the air quality of Zurich airport. Atmospheric Environment 41, 103-118.

Shi Y, Zhang N, Gao J, Li X, Cai Y (2011) Effect of firework display on perchlorate in air aerosols during the Spring Festival. Atmopheric Environment 45, 1323-1327.

Stedman J.R., Kent A.J. Grice S., Bush T.J., Derwent R.G. (2007): A consistent method for modeling PM10 and PM2.5 concentrations across the United Kingdom in 2004 for air quality assessment. Atmospheric Environment 41, 161-172.

Stohl A (2008) The travel-related carbon dioxide emissions of atmospheric researchers. Atmos Chem Phys, 8, 6499-6504.

Tan PH, Chou C, Liang JY, Chou CCK, Shiu CJ (2009) Air pollution "holiday effect" resulting from the Chinese New year. Atmospheric Environment 43, 2114 – 2124.

UNEP (2011) Environmental Assessment: Beijing 2008 Olympic Games.

Vecchi R, Bernardoni V, Cricchio D, DÁlessandro A, Fermo P, Lucarelli F, Nava S, Piazzalunga A, Valli G (2008) The impact of fireworks on airborne particles . Atmospheric Environment 42, 1121-1132.

Viana M, Querol X, Alastuey A, Postigo C, Lopez de Alda MJ, Barcelo D, Artinano B (2010) Environment International 36, 527-534.

Viana M, Postigo C, Querol X, Alastuey A, López de Alda MJ, Barcelo D, Artinano B, Lopez-Mahia P, Garcia Gacio D, Cots N (2011) Cocaine and other illicit drugs in airborne particulates in urban environments: a reflection of social conduct and population size. Environmental Pollution 159, 1241-1247.

Wang W, Primbs T, Tao S, Massy Simonich S (2009) Atmospheric particulate matter pollution during the 2008 Beijing Olympics. Environ Sci Technol 43, 5314-5320.

WDCGG (2011): World Data Centre for Greenhouse Gases. http://gaw.kishou.go.jp/wdcgg/

WHO (2006) Air Quality Guidelines. Global Update 2005: WHO Regional Office for Europe.

WHO (1987) Air quality guidelines for Europe: WHO Regional Office for Europe.

WHO (2000). Air Quality guidelines for Europe, 2nd edition: WHO Regional Office for Europe (WHO Regional Publications, European Series, No. 91).

Working group on Benzene (1998) Council Directive on ambient air quality assessment and management. Position Paper Benzene. http://ec.europa.eu/environment/air/quality/legislation/assessment.htm

Working group on Particulate Matter (2004) Second position paper on particulate matter. http://ec.europa.eu/environment/archives/cafe/pdf/working_groups/2nd_position_paper_pm.pdf

Xing J , Zhang Y, S Wang S, Liu X, i Cheng S, Zhang Q, Chen Y, Streets DG, Jang C, Hao J, Wang W (2011) Modeling study on the air quality impacts from emission reductions and atypical meteorological conditions during the 2008 Beijing Olympics. Atmospheric Environment 45 (2011) 1786-1798

Zhang H, Rattanavaraha W, Zhou Y, Bapat J, Rosen EP, Sexton KG, Kamens RM (2011) A new gas-phase condensed mechanism of isoprene-NOx photooxidation. Atmospheric Environment 45, 4507-4521

Annex A. Trend Model

The Mann-Kendall test

For analyzing a possible trend in observed time series the non-parametric Mann-Kendall test (Gilbert, 1987) has been used. This test is particularly useful since missing values are allowed and the data need not to conform to any particular distribution. Moreover, as only the relative magnitudes of the data rather than their actual measured values are used, this test is less sensitive towards incomplete data capture and/or special meteorological conditions leading to extreme values.

In the trend analyses a *consistent set* of stations is used. Requirements for a consistent set are:

- for each year within the time period a minimum data coverage as defined in section 2.1 is required;
- annual data is available for at least 75% of the years within the time period.

These results of the trend analysis should be interpreted carefully as there might be a bias towards the regions with the highest station density. Similarly, the comparison between the station type might be hampered as the spatial distribution over Europe may differ.

The Mann- Kendall statistic *S* is defined as:

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} \operatorname{sgn}\left(x_j - x_k\right)$$

where

$$\begin{aligned}
\operatorname{sgn}(x_j - x_k) \quad &= 1 \qquad \textit{if } (x_j - x_k) > 0 \\
&= 0 \qquad \textit{if } (x_j - x_k) = 0 \\
&= -1 \qquad \textit{if } (x_j - x_k) < 0
\end{aligned}$$

x_j is the observable (concentration, number of exceedance days, exposure) in year *j*; *n* is the available number of years with a valid measurement. In other words, *S* is the number of positive differences minus the number of negative differences. If *S* is a large positive number measurements taken later in time tend to be larger than those taken earlier in time. Similarly, if *S* is a large negative number, this indicates a downward trend. The Mann-Kendall statistic is only calculated for consistent sets of stations. The trend is called significant when α < 0.10.

If a linear trend is present, the slope is estimated by Sen's non-parametric procedure (Gilbert, 1987). For each time series with *n* valid measurements a set of slope estimates Q_{jk} is computed for each of the *n*(*n*-1)/2 data pairs:

$$Q_{jk} = \frac{x_j - x_k}{j - k}$$

Sen's slope estimate equals the median of the *n*(*n*-1)/2 slope estimates.

Reference

Gilbert, R.O., 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York.

Annex B Recent publications on the assessment of the Eyjafjallajökull eruption

Bukowiecki N., P. Zieger, E.Weingartner, Z. Juranyi, M. Gysel, B. Neininger, B. Schneider, C. Hueglin, A. Ulrich, A. Wichser, S. Henne, D. Brunner, R. Kaegi, M. Schwikowski, L. Tobler, F. G. Wienhold, I. Engel, B. Buchmann, T. Peter, and U. Baltensperger (2011) Ground-based and airborne in-situ measurements of the Eyjafjallajökull volcanic aerosol plume in Switzerland in spring 2010. Atmos. Chem. Phys., 11, 10011–10030; doi:10.5194/acp-11-10011-2011.

Colette A., Favez O., F Meleux F., Chiappini L., Haeffelin M., Morille Y. , Malherbe L., Papin A., Bessagnet B., Menut L., Leoz E., Rouïl L. (2011) Assessing in near real time the impact of the April 2010 Eyjafjallajökull ash plume on air quality. Atmospheric Environment 45, 1217-1221.

Flentje H., H. Claude, T. Elste, S. Gilge, U. K¨ohler, C. Plass-D¨ulmer, W. Steinbrecht, W. Thomas, A. Werner, and W. Fricke. The Eyjafjallajökull eruption in April 2010 – detection of volcanic plume using in-situ measurements, ozone sondes and lidar-ceilometer profiles (2010) Atmos. Chem. Phys., 10, 10085–10092; doi:10.5194/acp-10-10085-2010.

Gasteiger J., S. Groß, V. Freudenthaler, and M. Wiegner (2011) Volcanic ash from Iceland over Munich: mass concentration retrieved from ground-based remote sensing measurements. Atmos. Chem. Phys., 11, 2209–2223; doi:10.5194/acp-11-2209-2011.

Schäfer K, W. Thomas, A. Peters, L. Ries, F. Obleitner, J. Schnelle-Kreis, W. Birmili, J. Diemer, W. Fricke,W. Junkermann, M. Pitz, S. Emeis, R. Forkel, P. Suppan, H. Flentje, S. Gilge, H. E.Wichmann,F. Meinhardt, R. Zimmermann, K. Weinhold, J. Soentgen, C. Münkel, C. Freuer, and J. Cyrys (2011) Influences of the 2010 Eyjafjallajökull volcanic plume on air quality in the northern Alpine region. Atmos. Chem. Phys., 11, 8555–8575; doi:10.5194/acp-11-8555-2011.

Schumann U, B.Weinzierl, O. Reitebuch, H. Schlager, A. Minikin, C. Forster, R. Baumann, T. Sailer, K. Graf, H. Mannstein, C. Voigt, S. Rahm, R. Simmet, M. Scheibe, M. Lichtenstern, P. Stock, H. Rüba, D. Schäuble, A. Tafferner, M. Rautenhaus, T. Gerz, H. Ziereis, M. Krautstrunk, C. Mallaun, J.-F. Gayet, K. Lieke, K. Kandler, M. Ebert, S.Weinbruch, A. Stohl, J. Gasteiger, S. Groß, V. Freudenthaler, M.Wiegner, A. Ansmann, M. Tesche, H. Olafsson, and K. Sturm (2011) Airborne observations of the Eyjafjalla volcano ash cloud over Europe during air space closure in April and May 2010. Atmos. Chem. Phys., 11, 2245–2279; doi:10.5194/acp-11-2245-2011

Thomas H. E. and A. J. Prata (2011) Sulphur dioxide as a volcanic ash proxy during the April–May 2010 eruption of Eyjafjallajökull Volcano, Iceland. Atmos. Chem. Phys., 11, 6871–6880; doi:10.5194/acp-11-6871-2011

See also the special issue of Atmospheric Environment (Volume 48, Pages 1-240, March 2012) on "Volcanic ash over Europe during the eruption of Eyjafjallajökull on Iceland, April-May 2010" edited by Baerbel Langmann, Lucas Alados Arboledas, Arnau Folch and Volker Matthias.